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The Multielemental Analysis of Drinking Water Using Proton-Induced X-Ray Emission (PIXE)

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16. ABSTRACT

A new, rapid, and economical method for the multielemental analysis of drinking water samples is described. The concentrations of 76 elements heavier than aluminum are determined using proton-induced x-ray emission (PIXE) technology. The concentration of sodium is evaluated using an atomic absorption approach.

Targets for PIXE analysis are prepared from aqueous samples using a new "vapor filtration" technique. Each target is bombarded with protons, supplied by a nuclear generator. The resulting x rays are observed with an energy-sensitive semiconductor detector and the data recorded and processed with an on-line computer. Excellent detection limits (0.1 to 100 ppb) are obtained for most of the elements heavier than silicon.

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THE MULTIELEMENTAL ANALYSIS OF DRINKING WATER USING PROTON-INDUCED X-RAY EMISSION (PIXE)

by

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Contract No. 68-03-2178

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THE MULTIELEMENTAL ANALYSIS OF DRINKING WATER
USING PROTON INDUCED X-RAY EMISSION (PIXE)

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The primary mission of the Health Effects Research Laboratory in Cincinnati (HERL) is to provide a sound health effects data base in support of the regulatory activities of the EPA. To this end, HERL conducts a research program to identify, charcterize, and quantitate harmful effects of pollutants that may result from exposure to chemical, physical, or biological agents found in the environment. In addition to valuable health information generated by these activities, new research techniques and methods are being developed that contribute to a better understanding of human biochemical and physiological functions, and how these functions are altered by low level insults.

This report describes a rapid and economical method for the simultaneous determination of 76 elements in aqueous samples. The occurrence data, provided by this multielemental approach, will afford a sound basis for future epidemiological and toxicological studies.

R. J. Garner
Director
Health Effects Research Laboratory

ABSTRACT

Proton Induced X-ray Emission (PIXE) was used in this research program to provide analysis of drinking water samples for 76 elements heavier than aluminum. Atomic absorption was used for sodium analysis. A new technique called "vapor filtration" was used to prepare suitable targets for PIXE analysis from aqueous samples. Excellent detection limits (0.1 to 100 ppb) were obtained for most elements heavier than silicon. Energetic protons were provided by a nuclear accelerator, the x rays were observed with an energy sensitive semiconductor detector, and the data were recorded and processed with an on-line computer. Advanced electronic systems and a high degree of automation were used to provide high quality, low cost analysis for 6200 samples. The experimental equipment and procedures are described. The results of the analysis of drinking water samples will be available from the Health Effects Research Laboratory of the U. S. Environmental Protection Agency.

This report was submitted in fulfillment of Contract No. 68-03-2178 by Purdue University under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period February 24, 1975 to April 29, 1977, and work was completed as of April 26, 1977.

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ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

C	--	centigrade
C_v	--	coefficient of variation or relative standard deviation
DL	--	detection limit of an element
eV	--	electron volt
keV	--	thousand electron volts
l	--	liter
MeV	--	million electron volts
ml	--	milliliter
PIXE	--	proton-induced x-ray emission
ppb	--	part per billion
ppm	--	part per million
s	--	estimate of the standard deviation of replicate observations
μa	--	microampere
μC	--	microcoulomb
μg	--	microgram
Z	--	atomic number

SYMBOLS

Ac	actinium	Fe	iron	Ni	nickel	Si	silicon
Ag	silver	Fr	francium	Np	neptunium	Sm	samarium
Al	aluminum	Ga	gallium	O	oxygen	Sn	tin
As	arsenic	Gd	gadolinium	Os	osmium	Sr	strontium
At	astatine	Ge	germanium	P	phosphorus	Ta	tantalum
Au	gold	H	hydrogen	Pa	protactinium	Tb	terbium
Ba	barium	Hf	hafnium	Pb	lead	Tc	technetium
Bi	bismuth	Hg	mercury	Pd	palladium	Te	tellurium
Br	bromine	Ho	holmium	Pm	promethium	Th	thorium
C	carbon	I	iodine	Po	polonium	Ti	titanium
Ca	calcium	In	indium	Pr	praseodymium	Tl	thallium
Cd	cadmium	Ir	iridium	Pt	platinum	Tm	thulium
Ce	cerium	K	potassium	Pu	plutonium	W	tungsten
Cl	chlorine	La	lanthanum	Ra	radium	U	uranium
Co	cobalt	Li	lithium	Rb	rubidium	V	vanadium
Cr	chromium	Lu	lutecium	Re	rhenium	Y	yttrium
Cs	cesium	Mn	manganese	Rh	rhodium	Yb	ytterbium
Cu	copper	Mo	molybdenum	Ru	ruthenium	Zn	zinc
Dy	dysprosium	N	nitrogen	S	sulfur	Zr	zirconium
Er	erbium	Na	sodium	Sb	antimony		
Eu	europium	Nb	niobium	Sc	scandium		
F	fluorine	Nd	neodymium	Se	selenium		

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K. A. Mueller has been responsible for the direct supervision of the target preparation and analysis staff during this project. He has also made many creative contributions to the development of PIXE analysis for aqueous samples. The operation and maintenance of the accelerator has been supervised by B. D. Michael. A. M. Sills has made valuable contributions to the accelerator operations and target preparation. H. E. Haldman has been responsible for the operation of the electronic systems and the on-line computer. K. E. Melson and D. L. Coppage have exhibited an unusual degree of scientific skill and perseverance during thousands of hours of computer assisted analysis.

The atomic absorption measurements were conducted under the supervision of I. E. Smiley and K. J. Yost of the Purdue Bionucleonics Department.

N. S. Ulmer, Project Officer, has played an active role in this research project. She has understood the scientific and technical problems which are inevitable in a new development of this type and has made many constructive suggestions for improvements.

SECTION I

INTRODUCTION

GENERAL PRINCIPLES OF PIXE ANALYSIS

The potential for using energetic protons from a nuclear accelerator to perform quantitative, multielemental analysis was first discussed by Johansson, Akselsson, and Johansson (1). An excellent review of PIXE analysis has been written by Johansson and Johansson (2). When a sample is bombarded with protons, characteristic x rays emitted from each element heavier than magnesium can be used in uniquely identifying the element in the sample. The x rays are detected by an energy sensitive semiconductor device and the data are processed by an on-line computer. Proton excitation provides much better sensitivity than electron excitation because the yield of characteristic x rays compared to background radiation is much higher. Proton excitation has an advantage over x-ray excitation since good sensitivity can be obtained for a much larger group of elements in a single measurement.

A thorough discussion of the probability for characteristic x-ray production and the various types of background radiation that are produced has been given by Folkmann, Gaarde, Huss, and Kemp (3). The most important factors will be summarized here to show why PIXE provides excellent sensitivity for a very broad range of elements. The probability for characteristic x-ray production is very large in the energy region where the background radiation is maximum. This relationship is illustrated in Figures 1 and 2. Figure 1 shows the number of K and L x rays detected in our experimental arrangement as a function of the atomic number (Z) of the target atom. (The data were obtained using an absorber in front of the x-ray detector. Absorber selection is discussed in section 6.) Elements lighter than cerium (Z = 58) are detected by K x rays while L x rays are used for the heavier elements. Figure 2 shows a simplified representation for the intensity of background radiation as a function of x-ray energy. Energetic protons passing through the target knock out showers of electrons. When these electrons stop in the target, they produce a continuous x-ray spectrum called Bremsstrahlung or braking radiation. The x-ray detector is also slightly sensitive to nuclear γ rays which produce a small, continuous background over the total energy range of interest. The positions at which the characteristic x rays would appear in the spectrum are shown for a few typical elements by the vertical arrows. For example, chromium x rays occur near the peak of the Bremsstrahlung, but the yield for chromium x rays is very large as shown in Figure 1. On the other hand, the x-ray yield for cadmium is small, but the x rays occur at much higher energy than the

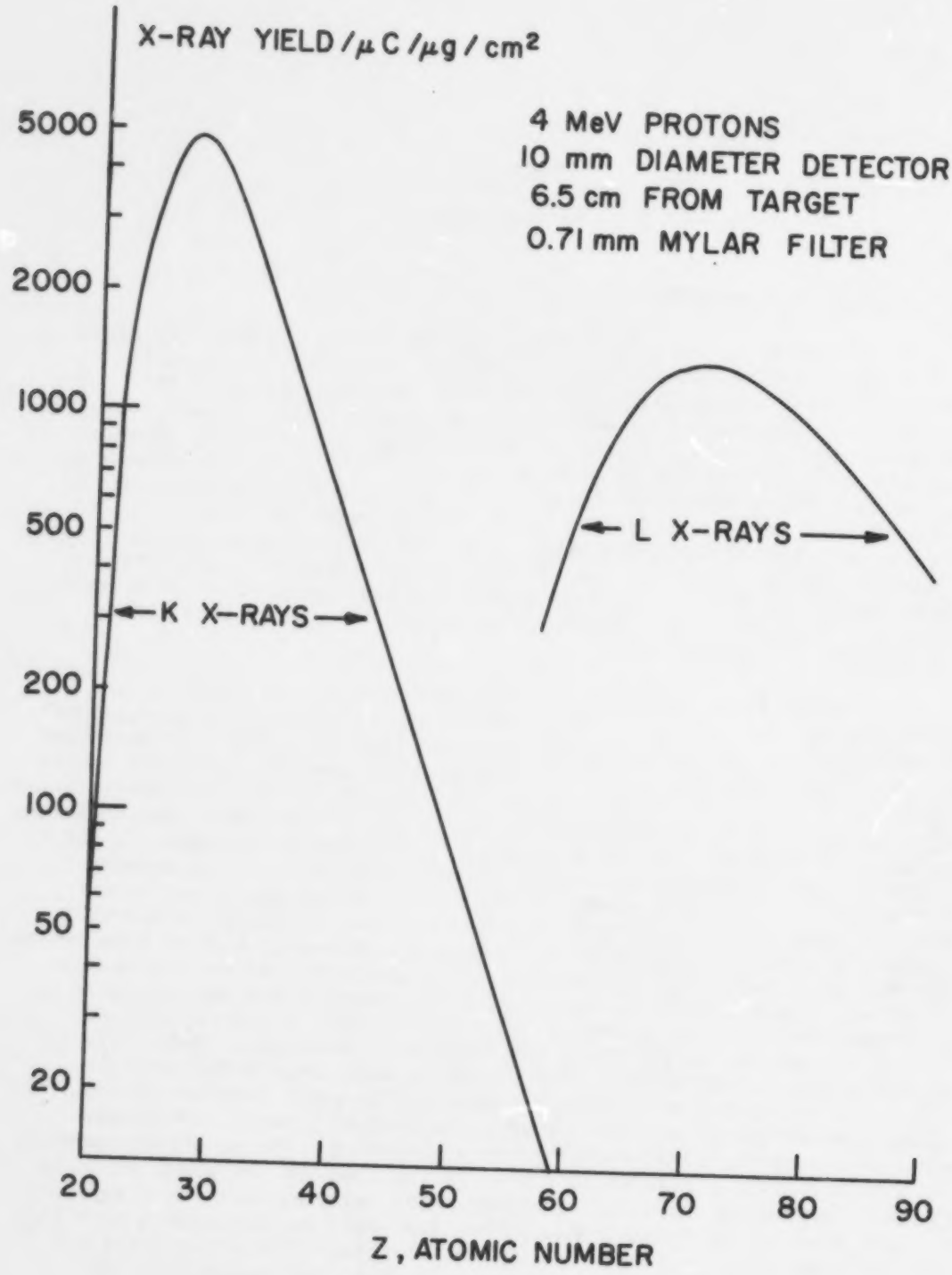

Figure 1. X-ray yield for PIXE analysis.

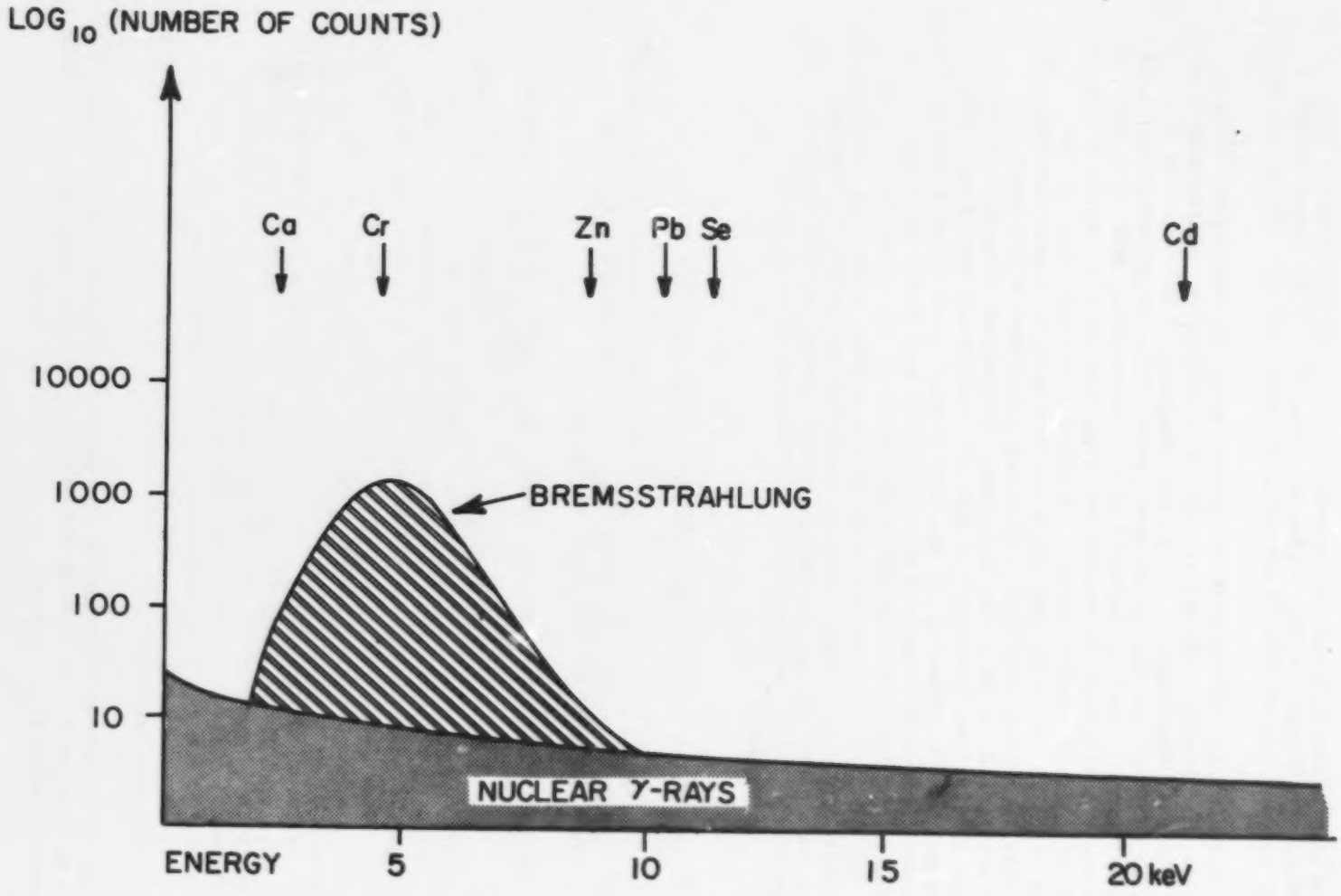

Figure 2. Typical background seen in PIXE analysis.

Bremsstrahlung where there is only a very small γ-ray background. The sensitivity for elements in the region of selenium and for heavy metals like lead is good because the x-ray yield is large and the background small.

It is useful to compare PIXE to optical emission techniques which are widely used for elemental analysis. The silicon-lithium semiconductor x-ray detector has many advantages. First, the response of the detector is essentially constant for months or even years. This is generally not true for photomultipliers used to detect light. Furthermore, PIXE uses only one detector while multielemental techniques employing optical emission have a separate detector for each element. In optical systems, most of the available light is not used, and the detectors must be preset for selected lines. This is unnecessary with PIXE since all x rays which reach the detector are stored in the x-ray spectrum. Unexpected elements can be identified and the characteristic x rays and background can be measured simultaneously. The intensity of the proton beam is measured directly during PIXE analysis; hence the excitation probability is a known quantity. Consequently, the background is measured directly, the detector is very stable, and the analytical calibration of the system is usually constant for long periods. Frequent comparisons to standards and reference samples, which are common for optical systems, are not needed in PIXE analysis. The characteristics of PIXE analysis will be discussed in more detail in sections 3, 4, 5, and 6.

TECHNIQUES DEVELOPED FOR PIXE ANALYSIS OF AQUEOUS SAMPLES

Although PIXE analysis has been used for a wide variety of samples (2), there were three areas that required extensive development before the technique could be used with aqueous samples:

1. A method was needed for depositing the elements from the aqueous sample on a thin backing suitable for proton bombardment. The procedure must recover extremely small quantities of material, and it must minimize the danger of introducing outside contamination.
2. A large quantity of data was needed to obtain extremely low detection limits for a wide range of elements. Since the time required for bombardment was the major factor in the cost of analysis, a high data rate was very desirable. We developed an "on-demand" pulsed proton beam and an advanced x-ray "pile-up" rejector that permits much higher x-ray counting rates than are generally available for PIXE analysis.
3. A more complicated computer program than that usually used for PIXE analysis was needed to provide the low detection limits and broad elemental range required. The new computer program is essentially automatic and requires minimum operator intervention; however, the operator is able to check the analysis quickly and make corrections if they are required.

A more complete description of the general principles of PIXE analysis is given in Section 3, and the procedures used for the analysis of drinking water samples under this contract are discussed in Section 6.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

The project has demonstrated that PIXE is a powerful tool for the multielemental analysis of drinking water samples. PIXE analysis provides excellent detection limits for a wide range of trace elements at relatively modest cost ($42.60 per sample in this project). PIXE is not the most sensitive method available nor the least expensive method if information is required for only a few elements.

It would be expensive to install PIXE analysis systems at laboratories that do not currently have a nuclear accelerator and a relatively large on-line computer. However, there are a large number of university and government laboratories which have most of the facilities needed for PIXE analysis. With some improvements in the Purdue University Accelerator Laboratory we could provide the quality of analysis demonstrated in this project for 20,000 samples per year at a cost-per-sample reduction of approximately 50 percent.

It would be easy to add the light elements, lithium, boron, fluorine, sodium, and magnesium, to the analysis by observing nuclear γ rays with a germanium-lithium detector at the same time that the x rays are detected. The sensitivity of PIXE analysis could be improved and the cost reduced by depositing larger quantities of the trace elements on the targets. The volume of water that can be processed by vapor filtration is limited by the quantity of calcium and sodium in the sample, so it would be desirable to study methods of removing at least part of these elements from the sample before vapor filtration.

In summary, it has been demonstrated that a nuclear accelerator can be used for large scale, multielemental analysis of drinking water. The full potential of the Purdue University accelerator for analyzing large numbers of samples was not utilized in the present work. The many suitable accelerators in the United States should be considered as a valuable national resource for large projects involving multielemental analysis in the areas of health effects, environmental control, mineral resource evaluation, and energy utilization.

SECTION 3

GENERAL DESCRIPTION OF TECHNIQUES AND PROCEDURES

SAMPLE PREPARATION

The process* described here was developed by the Purdue University Accelerator Laboratory staff prior to the award of U. S. Environmental Protection Agency (USEPA) Contract No. 68-03-2178. The process was included in the Purdue proposal submitted to the USEPA for "The Multielemental Analysis of Drinking Water Using Proton Induced X-ray Emission" and dated October 1, 1974.

A great improvement in sensitivity for trace element analysis of aqueous samples by PIXE can be obtained by eliminating the water before bombardment. In order to reach sensitivity levels of one part per billion (ppb) or better, approximately 30 ml of the sample must be reduced to dryness without significant addition or loss of trace elements. There are several problem areas in this process. First, the effects of kinetics must be minimized. For example, in a simple boiling process large amounts of material can be lost when drops of solution leave the surface of the sample. A similar effect occurs in freeze-drying processes as water vapor leaves the ice surface. Second, a closed system must be used to minimize contamination from outside sources. Third, one must quantitatively transfer the solids from the concentration unit to a suitable support. The apparatus must be easy to clean to prevent contamination from other samples. Finally, the trace elements in the sample may exist in various chemical forms, and the preparation technique must be independent of the chemistry of the sample.

We have developed a simple and novel solution to these problems (4). Consider a container whose bottom surface is a membrane permeable to water vapor but not readily permeable to water. The bottom surface of the membrane is exposed to a vacuum system. Water which approaches the vacuum side of the membrane immediately changes to the vapor phase, effectively depositing all solids on the membrane. The water vapor passing through the membrane is pumped away by the vacuum system. The membrane itself is then used as a target backing in PIXE analysis.

This concept, which we call "vapor filtration", has many attractive features. The water is not agitated, so there is no danger of water droplets spattering with subsequent loss of material. The kinetic motion of the water

*Purdue Research Foundation, Lafayette, Indiana, has filed a patent application (652,381) for the vapor filtration process.

moves the trace elements toward the desired deposit location. The system can be closed at the top so that airborne contaminants cannot enter. There is no final transfer of solids involved, so the process can be quantitative. Since no chemical processing is required, the process is not affected by the chemical composition of the dissolved or suspended solids.

There are five basic requirements for a practical vapor filtration device. 1) the membrane must pass water vapor, be reasonably strong, and contain minimal impurities. The device must provide 2) a good liquid seal between the membrane and the water container, 3) a good vacuum seal between the membrane and the vacuum system, and 4) a porous support so that the wet membrane will not break under atmospheric pressure. 5) The apparatus should be easy to clean.

Our solution for these requirements is shown in Figure 3. The water container is a cylindrical tube glued into a collar. The tube, which has an inside diameter of 1.6 cm, defines the area on the membrane where material from the sample will be deposited. The base has a recess to hold a porous polyethylene disk, a n-butyl O-ring seal to a vacuum port, and a lip on the outside top for easy alignment of the circular membrane and the water container collar. (The 15-mm, porous polyethylene column support disc, No. 275-264-0015, was purchased from Fisher and Porter Co., 1531 County Line Rd., Warminster, PA.) These pieces are made of General Electric Lexan polycarbonate plastic which is resistant to nitric acid and easy to clean. The collar and base are held together by a spring loaded aluminum clamp. The bottom of the collar and the top of the base must be carefully machined and polished to prevent water leaks on top of the membrane and vacuum leaks on the bottom. All parts of the vapor filtration apparatus were made in our laboratory machine shop. Medicine cups are used for the top cover. (General Medical Company, No. 721.)

A wide variety of materials were investigated to find a suitable membrane. The best material that is readily available commercially is DuPont PD 215 cellophane (2.3×10^{-2} mm thick). After the sample is dried, the membrane is mounted in a 35-mm, plastic photographic slide frame for bombardment. (The frames are manufactured by GEPE Garanti.)

The vacuum system has a number of requirements. The pressure on the vacuum side of the membrane must be kept below 4 Torr, the vapor pressure of ice at 0°C. Below this pressure it is impossible for water to exist in the liquid or solid phase. The disk that supports the membrane is sufficiently porous for the pressure at the membrane surface to be approximately 1 Torr. A mechanical pump will easily maintain this pressure, but it will not continually pump water vapor. Our pumping system consists of a large mechanical pump (Kinney Model KDH-130) whose outlet pressure is maintained at approximately 100 Torr by a water-ring pump (Kinney Model K-32-3). The water vapor is continuously pumped from the warm pump oil by the ring pump which is very efficient in the 100-Torr range.

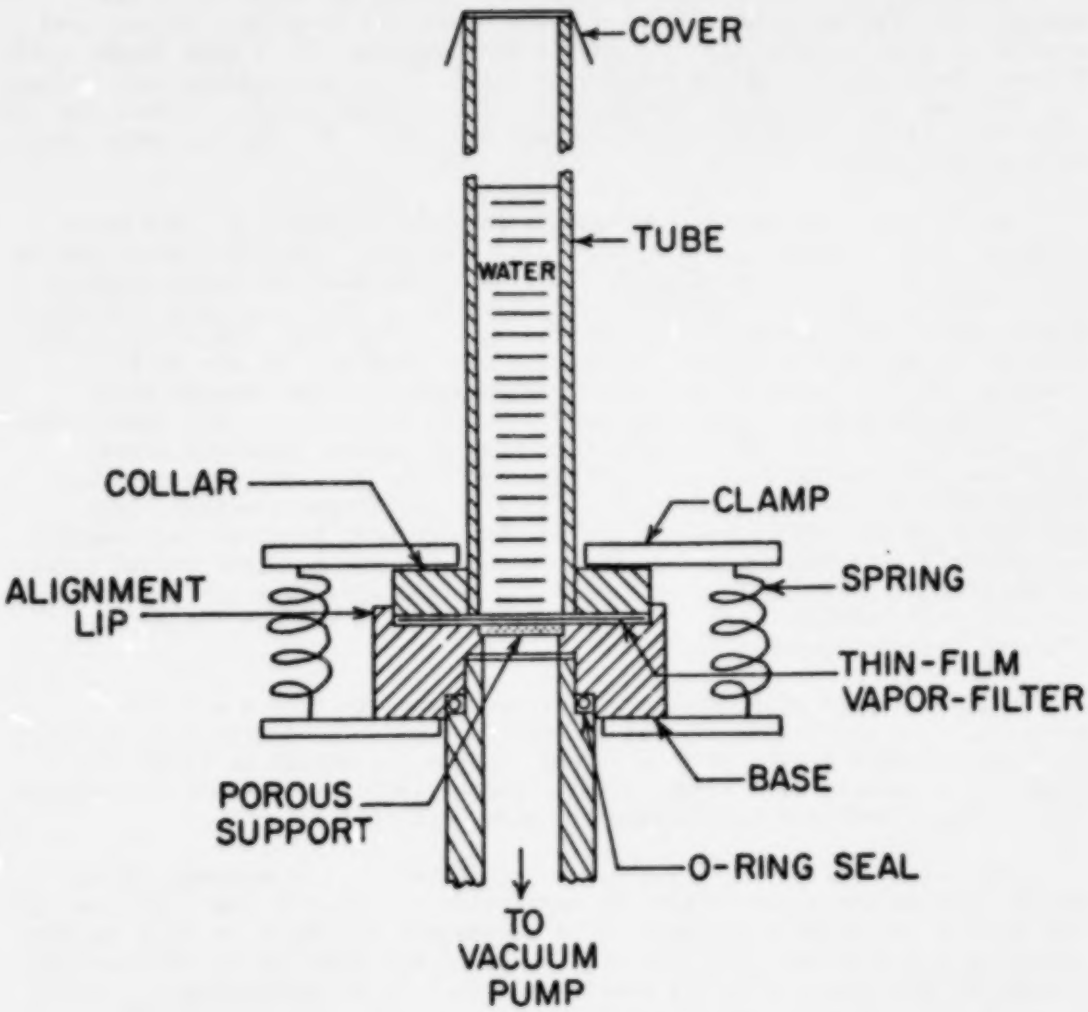

Figure 3. Vapor filtration apparatus.

Since approximately three days are required to pass each 30-ml water sample through the vapor filter, the vacuum manifold was designed to process 120 samples at the same time. The exact time required for drying each sample depends on the total dissolved solids in the sample. Prolonged pumping after the sample is dry weakens the membrane, so each pumping port has a separate vacuum shut-off valve. A less expensive pumping system could have been made with a small mechanical pump and a cold trap to condense water vapor. However, a large capacity pump is desirable so that good vacuum can be maintained even if a few membranes break during the drying cycle. The medicine cup which covers the top of the water container also aids in maintaining good vacuum. If a membrane breaks, the medicine cup forms a partial seal and limits the flow of air into the vacuum system.

Approximately five percent of the targets are not usable because of either a water leak, a membrane break during pumping, or a membrane tear during removal from the system. The membranes do not appear to be adversely affected by the normal nitric acid used to preserve samples (1.5 ml concentrated nitric acid per liter of sample), i.e., the breakage rate for acid preserved samples is essentially the same as that for pure water. However, some standard solutions prepared with other acids are difficult to process. For example, samples that contain aqua regia are very likely to damage the membrane. Also we have found that a small sample with a large concentration of acid is more likely to damage the membrane than a larger sample with the same quantity of acid.

The uniformity of the target depends on the type and quantity of material in the sample. There is a tendency for the deposit to be heavier around the edges of the target circle due to the meniscus at the end of the drying process. Target nonuniformity is not a major limitation as long as the proton bombardment is essentially uniform across the surface of the target.

A summary of the tests that have been performed to evaluate the quality of targets prepared by vapor filtration is given in Section 4.

BOMBARDMENT CHAMBER AND PROTON BEAM CONTROLS

Energetic protons are obtained from a High Voltage Engineering Model FN Tandem Van de Graaff Accelerator. The target is normally bombarded with a one-microamp (μa) beam of 4-MeV protons (approximately 6.3×10^{12} protons per second). The beam passes through a 2.5×10^{-3}-mm aluminum foil located 3 meters in front of the target to diffuse the beam and ensure that the proton bombardment is uniform over the target area. The beam is restricted to a 1.9-cm diameter circle by a series of tantalum collimators to ensure that the protons can strike only the sample and the thin cellophane support film. The beam spot is 3 mm larger than the target and 6 mm smaller than the target frame. Lead absorbers are used to prevent tantalum x rays produced in the collimators from reaching the x-ray detector.

A sketch of the target chamber is shown in Figure 4. Eighty targets are held in the circular slide tray of a modified 35-mm slide projector (Keystone, Model 1100). The target to be bombarded is dropped into the proton beam by the automatic mechanism of the projector. The protons pass through the target and are stopped on a carbon block located one meter behind the target so that Bremsstrahlung from the stopper cannot reach the x-ray detector. A 10-cm diameter plastic tube (not shown) extends from the back of the target down the exit beam pipe. This tube prevents scattered protons from striking metal components of the chamber and producing characteristic x-ray background.

X rays from the target go through a 0.025-mm Mylar window in the bombardment chamber and through a 0.025-mm beryllium window in the detector housing. These windows absorb most x rays emitted from elements lighter than aluminum. Several filters that can be changed from the computer are included to absorb high intensity x rays which would otherwise interfere with the detection of trace elements. The types of filters used for the measurements will be described in Section 6.

The detector is located 6.5 cm from the target. The axis of the circular detector is perpendicular to the surface of the target. In this geometry, the difference in the probability of detecting an x ray from the center and from the edge of the target is only 1.5 percent, so nonuniformity of the target cannot have a significant effect on the x-ray detection probability. In many other PIXE analysis systems the detector is located perpendicular to the beam axis at a 45° angle to the target. In that geometry the change in detection probability across the target would be 38 percent for the same target size and detector distance.

DETECTOR AND ELECTRONICS

The silicon-lithium detector (Kevex Model 3010 AR) is 1 cm in diameter and 3 mm thick. A 6-mm diameter mask is used in front of the detector to prevent x rays from interacting near the detector edges. This precaution is necessary to minimize the possibility that part of the x-ray energy will be lost from the detector by escaping electrons. The detector provides 170-eV energy resolution for 5.9-keV x rays. The system can respond to thousands of x rays per second, but even a few scattered protons per second will jam the detector-electronics system because the protons have approximately 1000 times as much energy as the average x ray. An absorber of at least 9×10^{-2} mm of Mylar is needed in the filter position to prevent scattered protons from reaching the x-ray detector.

Normally when an x ray is absorbed in the detector, all of the x-ray energy is converted into an electrical pulse. However, it is also possible for a silicon x ray, created in the detection process, to escape from the detector. These "silicon escape" events create extraneous peaks in the x-ray spectrum. For example, if a zinc K_α x ray strikes the detector and a silicon K_α x ray escapes, the event will appear to have almost exactly the same energy as the cobalt K_α x ray. It is possible for electrons released in the detection process to leave the surface of the detector. These events

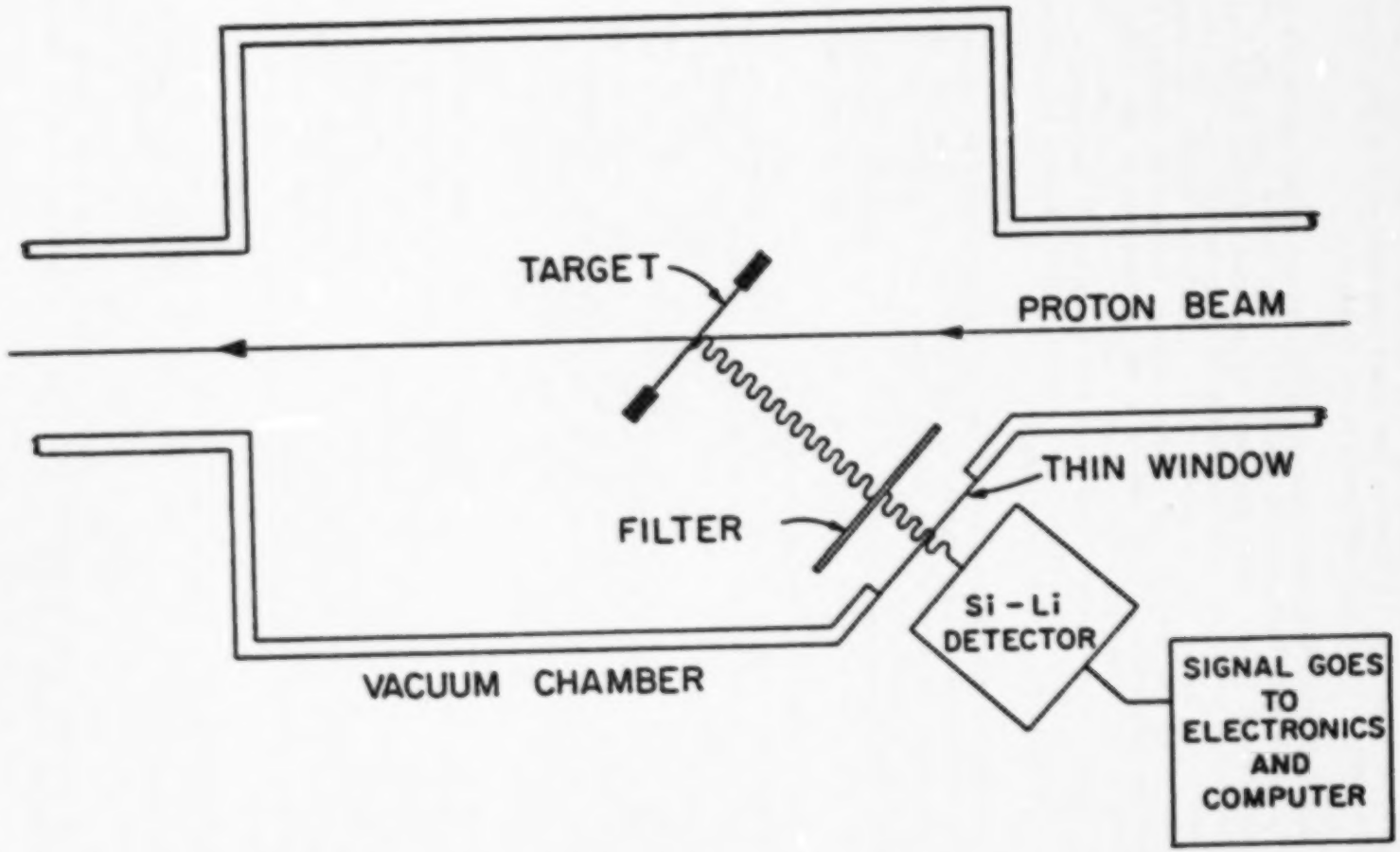

Figure 4. Schematic drawing of bombardment and detection apparatus.

produce a small tail on the low energy side of peaks in the x-ray spectrum. The computer must be able to correct for these two features of the detector response in order to get accurate analytical results.

The voltage pulse from the detector preamplifier is amplified and shaped by a Kevex Model 4532P Pulse Processor. Electronic noise from the detector is reduced in the 4532P processor by an active filter which has a 4-microsecond time constant. Approximately 50 microseconds are required to process each x-ray pulse. If a second x ray is detected before the energy of the first x ray has been stored in the computer processing circuit, both x rays must be discarded. If the second x ray is detected in the latter part of the first x-ray pulse, only the second x ray is lost. This effect imposes a serious limitation on conventional data taking systems. For example, if 10^4 x rays were hitting the detector per second, approximately 60 percent of the x rays would have to be discarded.

The problem of pile-up is greatly reduced in our system by switching the proton beam off the target approximately 1.5 microseconds after the first x ray is detected. As soon as the pulse processor has finished with an x-ray event, the beam is automatically returned to the target to produce a new x ray. With this "on-demand" beam pulsing system (5) there is typically only a 3 percent loss of data at an average rate of 10^4 x rays per second.

Even with the beam switching system there is still a small probability that a second x ray will be produced before the beam is removed from the target. When two x-ray pulses pile up in the noise filter, a single pulse is produced corresponding in energy to the summed energies of the two x rays. We have developed a circuit (6) that recognizes and rejects pile-up events unless the second x ray is emitted within T_r seconds of the first x ray. The resolving time of the pile-up detector (T_r) is approximately 0.1 microsecond for 2-keV x rays. T_r decreases as the x-ray energy increases. T_r is approximately 0.05 microsecond when the x-ray energy is greater than 6 keV. The undetected pile-up events are rare so they usually do not present a significant limit for the analysis.

The task of separating events that come from two x rays of similar energy is greatly simplified if the energy calibration of the electronic system is stable. The energy calibration is always a function of the counting rate in the detector. The Kevex Model 4532P pulse processor used in our system has correction circuits that limit the calibration variation to less than 0.03 percent for counting rates up to 10^4 x rays per second. The computer uses a large x-ray peak in the spectrum to make a fine adjustment of the energy calibration so that the energy uncertainty is less than 0.01 percent.

The proton beam is collimated so that all protons entering the target chamber must pass through the target. The total charge that is accumulated in the chamber during a measurement is recorded by a digital current integrator (Ortec Model 439) and stored in the computer. The quantity of charge on each proton is well known, so the computer converts the total charge into the number of protons passing through the sample. The computer also corrects for the number of events lost due to pile-up.

COMPUTER PROCESSING

On-line data accumulation and processing are performed by a Digital Equipment Corporation PDP-15/40 computer. The soft-ware currently used for PIXE analysis has required three years of development by Professor Frank A. Rickey. The analysis process is monitored and the computer is controlled with an interactive video display.

The first step in the analysis process is to subtract background radiation. Many experimental background spectra, each similar to the sketch shown in Figure 2, are stored on a magnetic disk. The operator selects a background spectrum which represents the host material of the target being analyzed. The computer adjusts the background to match the target including the effect of the peak-tails described above. The background is then displayed on the video monitor as an overlay on the experimental data. Usually, the computer generated background accurately describes the actual background from the sample, but the operator can instruct the computer to refine the background by contacting the display with a "light pen".

The computer also has stored experimental data that describe the shape and the position of the characteristic x-ray peaks in the spectrum. Even though the imperfections in the detector response are small, they can be important when there are intense x rays in the spectrum. The computer locates large peaks and identifies their tails and the peaks that are produced by silicon-escape x rays. Very large peaks can also produce simultaneous pile-up peaks. The computer performs a least-squares fit of the data to determine the number of x rays at each energy of interest. The stability of the energy calibration, the advanced knowledge of the shape of the characteristic x-ray peaks, and the careful treatment of imperfections and extra peaks are all essential factors for accurate analytical results.

The result of the least-squares fit is displayed on the video monitor as an overlay on the data. Most fitting errors are evident from a visual examination of the display, so the operator can instruct the computer with the light pen to refine the fit to the data. The most important part of a typical spectrum obtained for a water sample is shown in Figure 5. The vertical axis gives the number of x rays on a $\log_{10}$ scale and the horizontal axis gives the x-ray energy. Upon request the computer will expand any part of the spectrum so that the operator can examine details of the fit to the data.

After the visual examination, the computer makes additional checks on the analysis. The relative intensities of the major x rays emitted by each element in the unknown sample are compared to standard values which were determined from single element targets. Inconsistencies are reported to the operator. The computer also warns the operator of possible sources of error caused by two x rays with approximately the same energy.

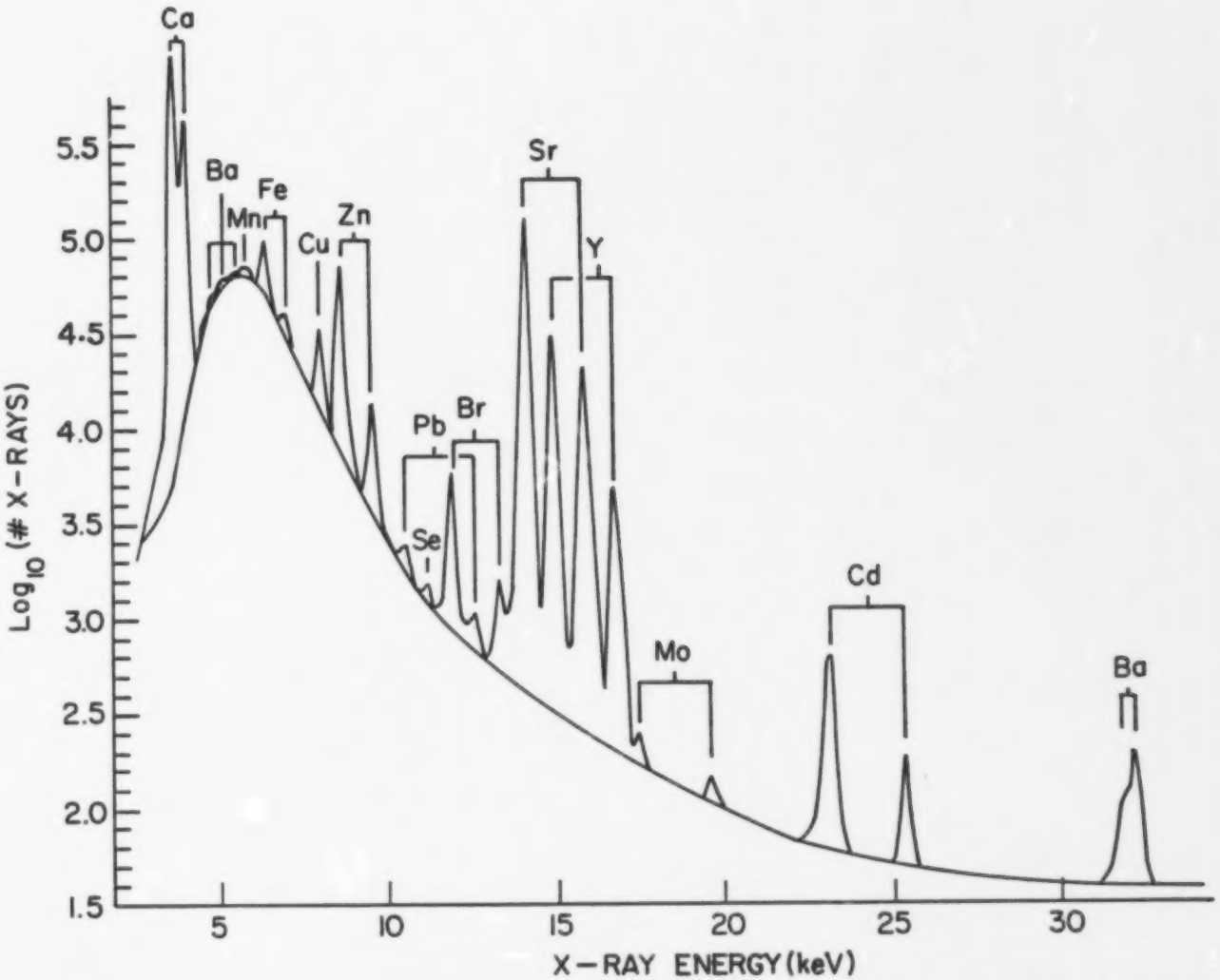

Figure 5. X-ray spectrum for a drinking water sample which has typical concentrations of most elements and a relatively large concentration of Cd.

Usually it is not necessary for the operator to intervene in the analysis; however, the following example will illustrate the steps that the operator can take should a question arise. Suppose that the computer had identified a large bromine and a small uranium component in the sample. The bromine $K_{\beta 2}$ intensity is reported as too small compared to the other bromine x rays. In addition, the uranium $L_{\alpha 1}$ x ray is reported as present, but the other uranium x rays are not clearly identified. This information indicates that the analysis is not correct because the bromine $K_{\beta 2}$ (13465 eV) x rays and the uranium $L_{\alpha 1}$ (13596 eV) x rays have similar energy. The operator would instruct the computer to delete uranium and refit those portions of the spectrum that contain any of the appropriate x rays. The computer now reports an intensity for bromine $K_{\beta 2}$ consistent with the other bromine x rays and a good fit to the data in all regions where uranium x rays would appear. The operator can be sure that the original fit had falsely assigned part of the bromine $K_{\beta 2}$ intensity to the uranium $L_{\alpha 1}$ x ray.

When the operator has approved the analysis of a sample, the computer uses the observed number of x rays and calculates the concentration of each element in the sample. The number of protons that have passed through the sample is recorded as units of charge, microcoulombs (μC), by the beam current integrator (Ortec Model 439). In a continuous beam system, a large correction would be required for the number of protons which passed through the target while the pulse processing system was busy. This correction is not necessary with our pulsed-beam system. A small correction (typically 3 percent) is made for the quantity of charge that was lost due to pile-up that occurred while the beam was being deflected from the target. Data for this correction is recorded automatically by an electronic scaler which counts the number of events that are rejected by the pile-up detector circuit. The x-ray yield per μC of protons for a given filter and proton energy are stored in the computer. (The procedure for obtaining this calibration is given in the following subsection.) The concentration, C, of each element in an individual sample is determined from the following equation:

$$C = N/YV$$

where

N is the number of characteristic x rays/μC
Y is the x-ray yield (number of characteristic x rays/μC/μg element)
V is the volume (liters) of sample analyzed

The final analytical results for the sample, including confidence limits, are printed on a single sheet of paper and stored on a magnetic tape for subsequent interpretation. The original data, the computer generated background, and the fit to the data are stored on a separate magnetic tape so the entire analysis can be checked should a question arise at a later time.

SYSTEM CALIBRATION

Calibration stability is a very important advantage of PIXE analysis. We will first summarize the most important points and then describe the details of the calibration.

1. It is not necessary to have a calibration standard for each element that is included in the analysis.
2. The source of excitation, i.e., the proton beam current, is measured directly.
3. In contrast to multielemental techniques which use optical emission, only one detector is used for PIXE analysis.
4. The detector is a semiconductor device whose characteristics usually are constant for several years.

The x-ray yield (Y_x) is defined as the number of x rays which are observed from a particular element during the bombardment of the target:

$$Y_x = N_A N_P P_E P_D$$

where:

N_A is the number of atoms of the element on the target.

N_P is the number of protons that pass through the target.

P_E is the probability of emitting an x ray of energy E_x.

P_D is the probability of detecting an x ray of energy E_x.

N_A, which is used to determine the weight of an element on the target, can be calculated from Y_x when the other factors are known. N_P is measured for each sample so it is a known quantity in the analysis.

P_E is a constant of nature. Statement (1) above is true because the change in P_E from element to element follows a smooth curve. The curve can be accurately defined by measuring Y_x for selected elements. The calibration for elements which are not included as standards can be obtained from the smooth curve. P_D has three components:

$$P_D = P_A \Omega_D \epsilon_D$$

where:

P_A is the probability that an x ray with energy E_x will pass through the absorber in front of the x-ray detector.

Ω_D is the solid angle of the x-ray detector.

ϵ_D is the probability that an x ray with energy E_x will deposit all of its energy in the x-ray detector.

For the type of absorbers used in this analysis, P_A is a smooth function of E_x. However, P_A can change during the course of the experiment if the surface of the absorber becomes coated with small particles and oil from the vacuum pumps. The factor, Ω_D, is constant because the detector is rigidly mounted, and ϵ_D is constant because it depends only on the volume of the x-ray detector.

Thin films with approximately 100 μg or less material per cm^2 were used to measure the x-ray yield curves so that it would not be necessary to correct for slowing down of the protons or x-ray absorption in the calibration material. Two types of calibration targets were used to provide a consistency check on calibrator preparation. Thirty-three calibration targets were obtained from Micromatter, Inc., 197 34th Avenue East, Seattle, WA, in the form of single elements or stable compounds vacuum-evaporated on Mylar backings. These targets are listed in column 3 of Table 1. Thirty calibrators were made in our laboratory from atomic absorption liquid standards. One ml of solution containing 100 μg of the calibration element was processed by vapor filtration to make each calibrator. These standards are listed in column 4 of Table 1. (The atomic absorption liquid solutions are more completely described in Table 2 in Section 4.)

The targets cover the range of elements from aluminum (Z = 13) to thorium (Z = 90). Forty-five elements are included in the calibration. Eighteen elements are present in both types of targets. Most elements in the atomic number range from 13 to 32 were included because the x-ray absorbers produce a relatively large curvature in the plot of the x-ray yield in this region.

The targets which are used for a particular calibration depend on the absorber which is present in front of the x-ray detector. (Absorber selection is discussed in Section 6.) For example, when an absorber is used to reduce the intensity of x rays from calcium, there is no point in analyzing x rays from elements lighter than calcium. These x rays would not pass through the absorber. Calibrators for calcium and heavier elements are used. The results of the x-ray yield measurements were fit with an algebraic function to obtain the smooth curve shown in Figure 1. (This curve is for $K_{\alpha 1}$ and $L_{\alpha 1}$ x rays. Similar curves are obtained for other less intense x rays for use in the consistency check of the x-ray intensity measurements described previously.) The results from individual calibrators are not shown in Figure 1 because most of the points would be so close to the line that it would be very difficult to evaluate the consistency of the calibration. Instead, Figure 6 shows in a much clearer form the data used to plot Figure 1. Each x-ray yield has been normalized by the corresponding value obtained from the best-fit function. The certified values of 10 of the calibrators were 8 or 9 percent lower than the values from the best-fit function. Two of the evaporated calibrators were obviously not correct. Since 46 other calibrators were very consistent, the 12 low calibrators were dropped from the best fit determination. The standard deviation of the 46 calibrators from the best fit function was 3 percent.

TABLE 1. ELEMENTS USED FOR X-RAY YIELD CALIBRATION

Element	Atomic number	Material used for evaporated film calibrators	Material used for vapor filtration calibrators
Aluminum	13	Al	
Silicon	14	SiO	
Sulfur	16	CuS	
Chlorine	17	NaCl	
Potassium	19	KCl	KCl
Calcium	20	CaF_2	$CaCO_3$
Scandium	21	Sc	$ScCl_3$
Titanium	22	Ti	Ti(in HCl)
Vanadium	23		V_2O_5
Chromium	24	Cr	$K_2Cr_2O_7$
Manganese	25		Mn(in HNO_3)
Iron	26	Fe	$FeCl_3$
Cobalt	27		Co(in HNO_3)
Nickel	28	Ni	Ni(in HNO_3)
Copper	29	Cu	CuO
Zinc	30	Zn	Zn(in HNO_3)
Gallium	31	GaP	$Ga(NO_3)_3$
Germanium	32	Ge	$(NH_4)_2GeF_6$
Selenium	34	Se	
Rubidium	37		RbCl
Strontium	38	SrF_2	$Sr(NO_3)_2$
Yttrium	39	Y	$Y(NO_3)_3$
Niobium	41	Nb_2O_3	
Molybdenum	42		Mo(in HNO_3 + HCl)
Palladium	46	Pd	$PdCl_2$
Silver	47		$AgNO_3$
Cadmium	48	Cd	Cd(in HNO_3)
Tin	50	Sn	Sn(in HCl)
Antimony	51		$SbCl_3$
Tellurium	52	Te	Na_2TeO_4
Iodine	53	CsI	
Cesium	55	CsI	
Barium	56		$BaCl_2$
Lanthanum	57	LaF_3	
Neodymium	60	NdF_3	
Gadolinium	64	Gd	
Erbium	68	Er	
Tantalum	73	Ta	
Tungsten	74		Na_2WO_4
Platinum	78		H_2PtCl_6
Gold	79	Au	
Thallium	81		Tl_2SO_4
Lead	82	Pb	Pb(in HNO_3)
Bismuth	83		Bi(in HNO_3)
Thorium	90	ThF_4	

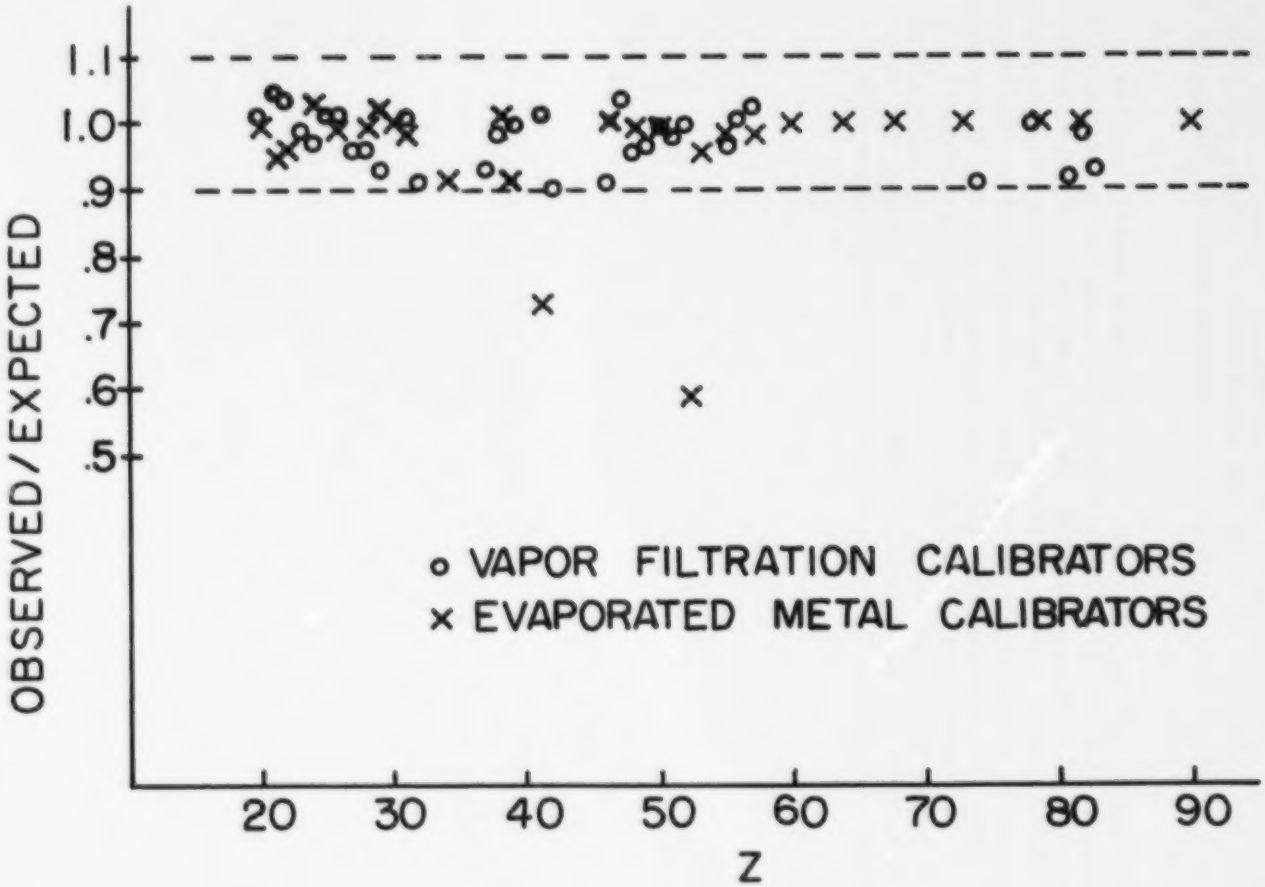

Figure 6. Comparison of evaporated calibrators and liquid single-element targets prepared by vapor filtration. The measured yields are divided by the values from a best-fit to all the calibrator points.

It is essential to understand the basic difference in the calibrations for PIXE analysis and optical emission analysis. If one uses an incorrect standard for optical emission analysis, the results for that element is affected directly. The calibration of a particular element in PIXE analysis, however, does not depend directly on the reliability of the target which contains that element. Each point on a calibration curve is determined by many elements.

The expressions given above for the x-ray yield reveals another important point. The calibration is reliable as long as the proton charge-measuring system is working correctly and the absorption probability is constant. These factors can be checked easily by using two single-element standard targets. A high energy x ray that is not effected by the absorber is used to check the accuracy of the charge-measuring system. A low energy x ray is used to ensure that the absorption probability is unchanged. We require that these tests agree with the calibration curve to within 3 percent. A variety of targets are alternated in these tests to minimize the danger that a mistake will be made if a particular target deteriorates with use.

SECTION 4

INITIAL EVALUATION OF PIXE ANALYSIS FOR AQUEOUS SAMPLES

Before the PIXE technique could be used for the analysis of drinking water, it was necessary to develop and test a method for preparing suitable targets from aqueous samples. Techniques such as freeze drying and various forms of evaporation were investigated and judged unsatisfactory because of the danger of trace material loss and contamination. The concept of vapor filtration that developed from these studies seemed very promising, but extensive development was required to refine the process. The tests described in this section were completed before the proposal was submitted for this contract.

It was demonstrated that water vapor would go through cellophane and other films at a reasonable rate. Even though cellophane is strong when it is dry, good mechanical support is required when it is wet.

The next step was to prove that the vapor filtration process was quantitative. The conditions and results of recovery measurements for the 35 elements of primary interest are summarized in Table 2. Most of the test solutions were prepared from commercial atomic absorption standards purchased from Fisher Scientific Co. and Alfa Division of Ventron Corp., as indicated in column 2 of the table. It was not possible to mix all of the standards in a single solution because of the various properties of the chemicals present. The 35 elements were divided into four groups as shown in column 3. A solution of each group of standards was prepared and diluted with ultra-pure water. The final elemental concentrations are shown in column 4. Nine aliquots, each 30 ml, were obtained from each of the four original standard mixtures. Targets were prepared and analyzed over a six-week period. Each recovery value in column 5 is the average of nine analyses. The standard deviation in column 6 should be interpreted in the usual way: the deviation of approximately two thirds of the measurements from the average was equal to or less than the specified value. The standard solutions were not held for longer than three months, so no attempt was made to evaluate their long term stability. During the period of the contract, analyses of fresh solutions of the same four groups of elements yielded results similar to those in Table 2.

The vapor filtration process is not sensitive to the chemical composition of the sample (except for volatile components and excessive acid in the sample). Therefore, the tests summarized above provide strong evidence that the vapor filtration process is an excellent method for preparing targets from aqueous solutions. Nevertheless, a number of additional tests were performed to evaluate problems that could occur due to large concentrations

TABLE 2. RECOVERY TEST FOR TARGETS PREPARED BY VAPOR FILTRATION FOR THE ELEMENTS OF PRIMARY INTEREST

Element	Source*	Group	Concentration µg/l	Average percent recovery†	Standard deviation†
Potassium	F	1	1000	96	6
Calcium	F	3	1000	97	5
Scandium	A	1	10	101	8
Titanium	F	2	10	96	5
Vanadium	F	2	10	99	4
Chromium	F	4	10	94	7
Manganese	F	3	10	102	5
Iron	F	2	10	103	6
Cobalt	F	3	10	94	8
Nickel	F	2	10	99	3
Copper	F	3	10	91	7
Zinc	F	3	10	99	5
Gallium	A	2	10	93	6
Germanium	A	4	10	91	7
Bromine	P	4	10	89	14
Rubidium	A	1	10	103	5
Strontium	A	2	10	93	4
Yttrium	A	3	10	100	3
Molybdenum	F	2	10	99	5
Palladium	A	1	10	98	7
Silver	F	3	10	92	8
Cadmium	F	3	10	97	5
Indium	A	1	10	95	6
Tin	F	1	10	93	6
Antimony	F	2	10	102	7
Tellurium	A	4	10	92	9
Iodine	P	4	10	56	16
Cesium	A	1	30	97	4
Barium	F	2	30	96	8
Lanthanum	A	1	30	93	8
Tungsten	A	4	10	92	5
Platinum	A	2	10	98	6
Thallium	A	1	10	101	8
Lead	F	3	10	99	4
Bismuth	F	3	10	88	9

*The standard solutions were obtained from Fisher Scientific Co. (F) and Alfa Division of Ventron Corp. (A). The test solutions for I and Br labeled (P) were prepared at Purdue University.

†Refer to the text for a description of the measurements and interpretation.

of sodium and calcium in drinking water samples. The four groups of standard solutions were added to drinking water samples which were collected in the Lafayette area. The recovery factors observed in these tests were similar to that shown in Table 2. Of course, the solids observed in the local water samples did not cover the elemental range that would occur in water samples from the proposed study, so the next step was to prepare test solutions which would simulate drinking water samples with large variations in calcium and sodium concentrations.

One obvious concern was the possibility of deposits being formed on the inner walls of the cylindrical tube during the vapor filtration process. Replicate 30-ml aliquots of samples containing 40, 80, 120, and 200 ppm of calcium were processed and analyzed. The average recoveries were 95, 101, 97 and 96 percent, respectively. Although the observed calcium recoveries were satisfactory, there was still the possibility that even a small calcium or sodium deposit might somehow trap a larger fraction of a trace component.

Solutions were prepared that contained from 0 to 200 ppm calcium or sodium and ppb concentrations of manganese, cobalt, nickel, copper, zinc, yttrium, silver, cadmium, lead, and bismuth. The results of the analyses of these solutions are presented in Table 3. The slightly lower recoveries for manganese, cobalt, copper, and nickel are probably the result of x-ray absorption rather than loss in the vapor filtration device. No significant loss can be attributed to the presence of sodium. Since the required accuracy of the analysis is 100 $\pm$ 10 percent, and very few drinking water samples contain 200 ppm concentrations of calcium these tests demonstrate that calcium and sodium deposits do not present a significant limitation on the analysis of these 10 elements.

While investigating the possible effects of calcium and sodium on the other 25 trace elements, solubility problems occurred when calcium concentrations of 80 ppm or greater were added to the solutions of trace elements. Typically only 80 percent of each element, including calcium, was recoverable. To determine whether the elements were retained on the wall of the cylindrical tube, a 30-ml aliquot of ultra-pure water was processed through each tube before it was cleaned. No significant concentrations of calcium or trace elements were observed in the analyses of these "rinse" samples. The missing material probably precipitated from solution during the process of combining the component solutions.

X-ray absorption is not expected to be significant for the analysis of elements heavier than calcium. A simple consideration of solubility suggests that the major components would precipitate first. The trace components would be located near the surface of the deposit, so x-ray absorption would be small. The data in Table 3 indicate this is the case. For example, if all the manganese in a 30-ml sample with 200 ppm of calcium is deposited under the calcium, 70 percent of the manganese K_{α} x rays would be absorbed. Since approximately 90 percent of the expected manganese was observed, it is evident that most of it was deposited on top of the calcium. The x-ray absorption probability of sodium is much smaller than for calcium, so absorption effects are expected to be smaller for sodium than for calcium. This trend is evident in Table 3.

TABLE 3. PERCENT RECOVERIES OF TRACE ELEMENTS IN PRESENCE OF VARIOUS CONCENTRATIONS OF CALCIUM AND SODIUM*

Ca(ppm)	0	40	80	120	200
			50 ppb concentrations		
Mn	97(5)	97(5)	91(4)	92(4)	89(5)
Co	95(5)	96(4)	91(3)	93(2)	90(5)
Ni	97(5)	97(3)	93(3)	94(5)	92(5)
Cu	93(5)	94(4)	92(3)	92(3)	89(4)
Zn	97(5)	101(3)	94(3)	97(3)	96(4)
Y	100(4)	104(5)	97(3)	100(4)	99(4)
Ag	99(5)	97(4)	101(5)	99(3)	98(4)
Cd	96(4)	95(5)	93(4)	96(4)	92(5)
Pb	98(5)	100(4)	94(4)	96(3)	96(3)
Bi	97(3)	96(3)	91(5)	94(5)	97(3)
			5 ppb concentrations		
Mn	105(5)	87(5)	95(3)	91(5)	88(5)
Co	96(5)	89(5)	99(5)	96(3)	91(4)
Ni	90(5)	88(5)	101(5)	96(4)	93(5)
Cu	92(5)	91(5)	94(4)	91(5)	90(5)
Zn	102(5)	99(5)	100(5)	105(5)	97(3)
Y	98(4)	92(5)	102(5)	98(5)	97(4)
Ag	92(5)	91(5)	98(5)	96(5)	95(5)
Cd	93(4)	93(4)	99(3)	94(3)	96(4)
Pb	102(4)	95(5)	100(3)	99(4)	97(5)
Bi	97(3)	101(4)	95(3)	98(4)	98(4)
Na(ppm)	0	40	80	120	200
			5 ppb concentrations		
Mn	100(3)	97(4)	96(4)	95(3)	98(3)
Co	96(5)	99(4)	92(5)	94(3)	96(4)
Ni	100(4)	97(3)	95(3)	98(4)	100(4)
Cu	92(5)	93(5)	89(4)	92(5)	93(3)
Zn	101(4)	98(3)	97(4)	104(5)	98(3)
Y	99(3)	96(4)	96(3)	102(4)	97(4)
Ag	98(3)	101(3)	98(4)	92(5)	96(5)
Cd	96(4)	91(5)	98(3)	94(3)	95(3)
Pb	98(4)	95(5)	98(3)	99(3)	97(4)
Bi	94(4)	97(3)	91(3)	95(5)	96(3)

* Each number in parenthesis represents the standard deviation of the observations of percent recovery.

Since the probability of x-ray absorption increases as the x-ray energy decreases, additional tests were performed to determine the recovery of elements lighter than manganese. A series of solutions containing 200 ppm calcium and 50 ppb of a single element were analyzed. The recoveries of vanadium, titanium, and chromium were 91, 89, and 95 percent, respectively. The recovery of even lighter elements was much poorer; e.g., for sulfur it was as low as 30 percent.

Analyses of drinking water samples containing 30 to 80 ppm calcium and sodium concentrations were also performed to evaluate their effects on the recovery of light elements. Targets were made from one-ml and 30-ml samples to provide a large difference in the total material on the target. The observed intensity of x rays from potassium and sulfur, normalized for sample volume, was much smaller from the 30-ml samples than from the one-ml sample. This confirmed the conclusion that x-ray absorption is a serious problem in the analysis of light elements.

In principle it would be possible to correct for x-ray absorption if one knew how the material was deposited on the target. Since absorption can be large for light elements and there can be large variations in the formation of target deposits, we concluded that one-ml samples should be used for the analysis of the following light elements: phosphorus, sulfur, chlorine, potassium, and calcium. The advantage of the one-ml target is simple; even in the extreme case of phosphorus totally covered by the deposit from 200 ppm of calcium, the x-ray absorption would only be 13 percent.

The dissolved solids in the sample also influence target reliability. Since material might fall from the backing when the target deposit was heavy, drinking water samples and samples made from known solutions with high concentrations of calcium and sodium were evaluated. Three aliquots of each sample were prepared and analyzed. One target was coated with a clear plastic film from an aerosol spray can (Borden Number 1302). One uncoated target was handled very carefully and another uncoated target was shaken with the sample surface down. Targets with blank cellophane backing were also sprayed with plastic and analyzed to correct for the components in the plastic film. The results of these tests showed that there was no detectable loss of material as long as the total material on the target backing was less than 5 mg. (A 30-ml sample with a 167-ppm calcium concentration would produce a 5-mg deposit.) All of the analyses reported here and furnished in the drinking water study were performed on uncoated targets, and there is no evidence that the vapor filtration targets require more than normal care in handling.

Since PIXE analysis depends on the comparison of x-ray yields from relatively thick targets to yields from thin calibrators, it is necessary to evaluate the effect of slowing down the incident protons in the target. The average energy of a proton going through a target prepared from a 30-ml sample containing 50 ppm of calcium and 50 ppm of sodium would be approximately 3.95 MeV rather than 4 MeV. The variation in x-ray yield as a function of proton energy is not the same for all elements, but it is typically only 30 percent per MeV. If the deposit on the target is uniform, the change in yield as the proton slows down would be only 1.5 percent.

Unless the targets are extremely nonuniform, this correction would be insignificant. The recovery evaluation data, given in Table 3, were not corrected for a decrease in proton velocity, so it does not appear that the nonuniformity of the targets is large enough for this effect to be significant.

SECTION 5

PRECISION AND DETECTION LIMITS

DEFINITIONS

The statistical interpretation of multielemental data requires an evaluation of the magnitude and sources of variability in the elemental observations. Since replicate observations of each element will be normally distributed about some mean with a variance, σ^2, the magnitude of the variability of the replicate determinations of each elemental concentration can be expressed in terms of σ, the standard deviation or square root of variance. In this research the variability is actually presented in terms of s, the estimate of the standard deviation, and C_v, the coefficient of variation or relative standard deviation. These terms are derived as follows:

$$s = \left[\sum_{j=1}^{n} \frac{(C_j - \bar{C})^2}{n - 1} \right]^{1/2}$$

and

$$C_v = 100\ s/\bar{C}$$

where:

C_j = individual observed elemental concentration (μg/l)
$\bar{C}$ = mean of the individual observed elemental concentrations (μg/l)
n = number of replicate observations of the elemental concentration

Attention is now directed to the sources of variability in the elemental observations. Two of the most significant sources of variability are the counting and instrumental effects. Interelemental effects may also occur and introduce additional variabilities.

The counting variance, s_c^2, is a measure of the variability in the emission of x rays from a sample. Since the emission of x rays follows a Poisson distribution, the best estimate of the numberical value of the counting variance, expressed in $(\mu g/l)^2$, is derived from $\bar{N}$, the mean number of characteristic x rays/μC; Y, the x-ray yield or number of characteristic x rays/μC/μg element; and V, the volume of sample expressed in liters. Thus,

$$s_c^2 = \bar{N}/(YV)^2$$

If the total number of characteristic x rays emitted from an element is large, however, the variance may be estimated from one count without performing a series of counts and calculating a mean count.

The instrumental variance, s_i^2, is a measure of the variability of the function of the components of the instruments, such as the proton beam and the detector. Since the function of the instrumental components follows an unknown distribution, the best estimate of the instrumental variance, expressed in $(\mu g/l)^2$, is derived from s_N^2, the variance of replicate observations of N, the number of observed characteristic x rays/μC; Y, the x-ray yield; and V, the volume of sample, expressed in liters. Thus,

$$s_i^2 = s_N^2/(YV)^2$$

The counting and instrumental effects are independent of one another. If the interelemental effects are considered negligible, then s^2, the estimate of the variance of replicate observations of the elemental concentration, may be expressed as follows:

$$s^2 = s_c^2 + s_i^2$$

Since s, the standard deviation expressed in $\mu g/l$, may be estimated by deriving the square root of the variance, then

$$s = (s_c^2 + s_i^2)^{1/2}$$

When the number of individual elemental observations is large, the proportion of total observations lying within any given range about the mean of the observations is related to the standard deviation. Thus, 68 percent of the observations lie within $\bar{C} \pm 1$ s, 95 percent within $\bar{C} \pm 2$ s, and 99 percent within $\bar{C} \pm 3$ s. In this research the confidence limits, $\bar{C} \pm 1$ s, were employed.

The detection limit, DL, is generally interpreted as the smallest concentration of an element that can be observed with reliability. However, there seems to be no general agreement on the definition of "reliability." The procedure used in this work can be described in terms of the probability distributions shown in Figure 7. The detection limit was set equal to σ, the theoretical standard deviation. When the actual concentration of an element is zero or equal to DL, the concentrations observed in repeated measurements would follow distribution A or B, respectively. From Figure 7 it is evident that the probability of obtaining an observed concentration between zero and DL is the same when the actual concentration is zero or equal to DL. Thus observed concentrations in this range are unreliable and are not reported. On the other hand, only 16 percent of distribution A exceeds DL. Any observed concentration, C_o, which is larger than DL is considered reliable because there is at least an 84 percent probability that the element is present in the sample. Given the fact that 50 percent of distribution B exceeds DL, the detection limit is the smallest concentration of an element that is needed to have a 50 percent probability of obtaining a reliable value for C_o. The sample standard deviation, s, will be used as the best estimate for σ, that is the detection limit.

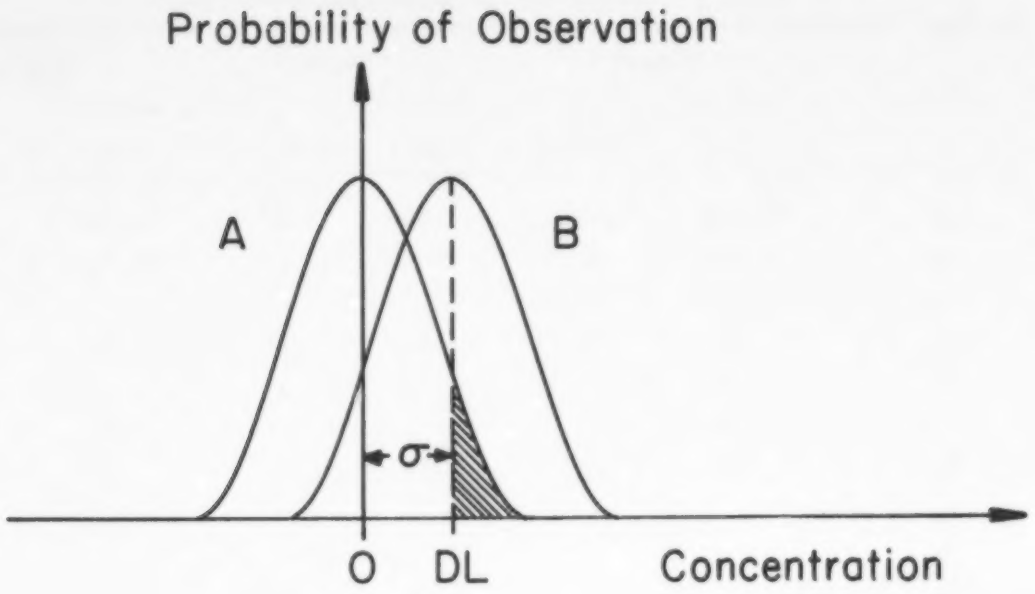

Figure 7. Sketch of probability distributions used to define detection limits.

EVALUATION AND DISCUSSION

Now that the terms for statistical interpretation have been defined, the procedures used to determine the magnitude of the variability of the observations of elemental concentration will be described. A number of drinking water samples, collected from local public water supplies and home wells, were analyzed. Calculations were then performed to determine the standard deviation of the observations of each of the 10 elements present in sufficient concentration for 1) s_c, the estimate of the counting standard deviation, to be less than 3 percent of $\bar{C}$, the mean of the elemental observations, and 2) the interelemental effects to be negligible. (Use of the 3 percent value assured that the counting variance was less than 10 percent of the instrumental variance as shown below.) The results of the replicate analyses of three typical samples are given in Table 4. Examination of the data reveals that the average percent coefficient of variation or relative standard deviation was about 10. Consequently, the magnitude of the confidence limits assigned to each elemental concentration observed thereafter was 10 percent of the observation, i.e., $C_j \pm 1$ s or $C_j \pm 0.1\ \bar{C}$. These limits can only be considered approximations, however, since they were derived from observations of a limited number of elements in a few samples from one geographical area and then applied to a single observation of each element in each sample.

TABLE 4. EVALUATION OF ANALYTICAL PRECISION

Element	Sample 1		Sample 2		Sample 3	
	Average* (ppb)	C_v (Percent)	Average* (ppb)	C_v (Percent)	Average* (ppb)	C_v (Percent)
K	2,100	12	1,900	9	1,100	10
Ca	24,000	8	7,600	6	53,000	9
Ti	14	9				
Fe	76	8	104	10	14	9
Cu	43	7	29	9		
Zn	36	11			19	9
Sr	84	10	39	9	168	9
Mo					17	11
Ba	56	8			107	12
Pb			9	10		

*Five targets were analyzed for each sample.

The relative significance and magnitude of the counting and instrumental variances may be derived after dividing the second of the previously cited equations for s^2, the variance of the replicate observations of elemental concentrations, by $\bar{C}^2$, the square of the mean of the observed elemental concentrations. Thus,

$$s^2/\bar{C}^2 = s_c^2/\bar{C}^2 + s_i^2/\bar{C}^2$$

When the percent coefficient of variation is 10 (i.e. $s = .1\ \bar{C}$) and the counting standard deviation is 3 percent of the mean elemental concentration, the equation becomes

$$(0.1)^2 = (0.03)^2 + s_i^2/\bar{C}^2$$

$$\text{then} \quad s_i^2/\bar{C}^2 = (0.095)^2 \sim (0.1)^2$$

The magnitude of the instrumental variance is approximately the variance of the elemental observations, i.e., 10 percent of the mean concentration. The instrumental variance is, therefore, considered the primary factor in the variance of replicate observations of elemental concentration above the detection limit. As the mean of the observed elemental observations approaches the elemental detection limit, however, the value of the expression, $s^2/\bar{C}^2$, approaches unity since the detection limit is equal to s.

Therefore,

$$s_c^2/\bar{C}^2 + s_i^2/\bar{C}) \sim 1$$

Substituting the previously derived approximate value for $s_i^2/\bar{C}^2$, the relationship now becomes,

$$s_c^2/\bar{C}^2 + 0.01) \sim 1$$

The counting variance appears to become the most significant factor in the variance of the elemental observations as the latter approach the detection limits.

The magnitude of the counting variance may be estimated more specifically after considering the x-ray spectrum. As shown in Figure 5, the spectrum consists of peaks produced by monoenergetic, characteristic x rays and continuous background from Bremsstrahlung and nuclear gamma rays. In any particular peak, N_t, the total number of observed x rays/μC; N_p, the number of observed characteristic x rays/μC; and N_b, the sum of the numbers of observed background x rays and gamma rays/μC, are related as follows:

$$N_p = N_t - N_b$$

When the total number of observed x rays is large, the numerical values for s_t^2, s_b^2, and s_p^2, the corresponding variances of N_t, N_b, and N_p, each expressed in $(ug/l)^2$, may be estimated as follows:

$$s_t^2 = N_t/(YV)^2 = (N_p + N_b)/(YV)^2$$

$$s_b^2 = N_b/(YV)^2$$

$$s_p^2 = (N_p + 2\ N_b)/(YV)^2$$

(In these expressions, Y and V are defined as before.) The numerical value of s_c^2, the counting variance expressed in $(ug/l)^2$, then becomes

$$s_c^2 = s_p^2 = (N_p + 2\ N_b)/(YV)^2$$

When the elemental observations are near the detection limits and N_p is less than N_b, the numerical value of the counting variance expressed in $(ug/l)^2$ then approaches the following:

$$s_c^2 \sim 2\ N_b/(YV)^2$$

In actual practice a least-squares program is utilized to calculate the contribution of the counting variance to the variance of the observations of elemental concentration.

For the purpose of evaluating the detection limits of the various elements in targets prepared from 30-ml aliquots of sample containing 50 ppm calcium, a test target containing 1.5 mg calcium was bombarded under the same conditions used in the multielemental analyses of drinking water

samples. Then N_b, the sum of the observed numbers of background x rays and gamma rays per μC, was determined at the energy of each characteristic x ray that would be counted in the analyses. Since s^2, the variance of the replicate observations of the elemental concentration, was previously shown to approach s_c^2, the counting variance, then s, the standard deviation of the elemental observations expressed in $\mu g/l$ can be estimated from the following:

$$s \sim s_c \sim (2N_b/Y^2V^2)^{1/2}$$

Since DL, the detection limit, is set equal to s in this research, then the approximate value of DL can be derived as follows:

$$DL = s \sim (2N_b/Y^2V^2)^{1/2}$$

Attention is now directed to other factors which can effect detection limits and analytical precision. Although the material in the target deposit does not have a major effect on the Bremsstrahlung background, large quantities of sodium in the sample can have a dominant effect on the high-energy background. The probability of exciting emission from sodium nuclei during proton bombardment is relatively large. Most of the 440-keV rays from sodium do not interact with the x-ray detector, but a few will leave a small part of their energy in the detector, thus adding to the continuous high-energy background. Although the number of these events is small, the K x-ray yield for elements with atomic numbers between 46 and 57 is also small, so sodium can increase the standard deviation for these elements.

Large quantities of elements heavier than silicon can affect s in another way. As noted in the previous description of the detector and electronics, the x-ray counting rate is limited by the noise filter which is essential for good energy resolution. Thus the number of x rays that can be observed from trace elements in a fixed time period will be limited by intense radiation from an abundant element. Since analysis costs are directly related to bombardment time, the most practical solution is to reduce the intensity of the dominant radiation with an absorber. When any type of absorber is used, there will be some loss of x rays needed in the analysis. Hence a number of compromises must be made. The factors influencing the selection of the best absorber for drinking water analysis will be described in Section 6.

The finite energy resolution of the x-ray detector can also affect s for some elements. An intense x ray from an abundant element may have approximately the same energy as a low intensity x ray from a trace element. The standard deviation for that trace element will be limited to a fraction of the abundant element. This limitation is most common for rare earth elements. As shown in Figure 1, elements heavier than lanthanum (Z = 57) are detected by L x rays. The L x rays from rare earth elements occur in the same energy region as the K x rays from elements with atomic numbers from 24 to 30. The latter are frequently present in relatively large concentrations.

If the sum of the energy of simultaneous pile-up x rays is close to the energy of an x ray of interest, the standard deviation for that element can be increased. Our advanced pile-up detector minimizes the number of pile-up events in the x-ray spectrum, so this effect is rarely significant.

The problems caused by x rays of similar energy from different elements can be reduced by selecting the particular x rays used in the analysis. Elements heavier than calcium emit at least two x rays which are distinctly different in energy. Typically the K_β intensity is 20 percent of the K_α intensity. For many elements, the L_α and L_β x rays have approximately the same intensity. If one of these x rays is obscured by a stronger x ray, the other can be used for analysis.

The detection limits given in Table 5 were calculated using the background observed from a typical target as described previously. A restriction is placed on the detection limits for samples that have large concentrations of calcium. When the calcium concentration was greater than 50 parts per million (ppm), it was necessary to reduce the proton beam intensity to reduce the calcium x-ray counting rate. The detection limits for other elements were increased because fewer x rays were observed in the normal counting period.

The detection limits for elements lighter than scandium are relatively large because targets were made from one-ml samples. This procedure provided the detection limits required for the investigation and reduced the corrections necessary for the absorption of low-energy x rays in the sample material. This problem has been discussed in Section 4.

The variations in detection limits for adjacent elements are caused by a variety of effects discussed in previous sections of this report. Some examples of these effects will now be described. The detection limit for scandium is limited to 0.1 percent of the calcium concentration because the energy of the K_β x ray from calcium is close to the energy of the K_α x ray of scandium. The detection limits for titanium and vanadium are larger than that of chromium because the Mylar absorber used to reduce the calcium x rays also absorbs significant numbers of titanium and vanadium x rays. In addition, L x rays from barium, which are relatively abundant in some samples, occur in the same energy region as the x rays from titanium and vanadium.

The analysis of arsenic and lead present a good example of the use of alternate x rays to minimize the variability caused by x rays of similar energy. The difference in energy between the K_α x ray of arsenic and the L_α x ray of lead is only 2 eV, so it is impossible to distinguish between these two x rays. Fortunately, the $L_{\beta 1}$ x ray from lead is relatively intense and does not interfere with any common x rays, so it is used to detect lead. The intensity ratio of the lead L_α and $L_{\beta 1}$ x rays has been measured, so the lead contribution to the combined peak from lead and arsenic can be subtracted to determine the arsenic concentration. In principle, the K_β x ray from arsenic could also be used, but it is frequently obscured by relatively intense x rays from bromine in drinking water samples.

TABLE 5. DETECTION LIMITS* FOR PIXE ANALYSIS OF DRINKING WATER

Element	Detection Limit† (ppb)	Element	Detection Limit† (ppb)	Element	Detection Limit† (ppb)
Si	5000	Mo	1	Tm	3
P	500	Tc	1	Yb	3
S	100	Ru	1	Lu	3
Cl	100	Rh	1	Hf	3
K	100	Pd	0.1	Ta	3
Ca	100	Ag	1	W	0.3
Sc	3 or 0.1% Ca	Cd	0.1	Re	3
Ti	1	In	0.2	Os	3
V	1	Sn	0.3	Ir	3
Cr	0.1	Sb	0.4	Pt	0.3
Mn	1	Te	0.7	Au	3
Fe	1	I	1	Hg	3
Co	0.1	Cs	2	Tl	0.3
Ni	0.1	Ba	2.5	Pb	0.1
Cu	1	La	2.5	Bi	0.3
Zn	1	Ce	20	Po	3
Ga	0.1	Pr	18	At	3
Ge	0.1	Nd	16	Fr	3
As	0.5	Pm	13	Ra	3
Se	1	Sm	12	Ac	3
Br	0.1	Eu	11	Th	3
Rb	0.1	Gd	9	Pa	3
Sr	0.1	Tb	8	U	3
Y‡	0.1	Dy	7	Np	3
Zr	1	Ho	6	Pu	3
Nb	0.1	Er	5		

*The term detection limit is defined and discussed in the text.

†For samples with greater than 50 ppm of calcium, the cited detection limit is multiplied by the factor (calcium concentration in ppm)/50 ppm. This modification does not apply to scandium.

‡Since yttrium is used as an internal standard, it is not determined in the sample.

The effect of imperfections in the detector response can be illustrated with manganese. If the concentration of iron in the sample is very large, there will be a slight tail on the low energy side of the iron K_α x-ray peak. Since this makes it somewhat more difficult to determine the background under the manganese K_α x ray, the detection limit for manganese is not as good as for chromium.

The increase in detection limit for the elements between cadmium and lanthanum is caused by the steady decrease in the x-ray yield for these elements. The detection limits are larger for the rare earth elements because the analysis uses L x rays occurring in the energy region where the Bremsstrahlung is large.

Many of the other variations result from the economical use of computer time during the analysis. The time required to perform and evaluate the least-squares fit of the x-ray spectrum would be much longer if all elements were automatically included. If the computer time exceeds the bombardment time, the cost of analysis would be increased. As a practical compromise, the elements of primary interest listed in Table 2 were always included in the least-squares fit. The computer was programmed to recognize other peaks and add them to the analysis. Of course it is very difficult for the program to distinguish very small peaks from random variations in the background. To minimize computer time a relatively high detection limit was used for each secondary element.

It was necessary to bombard some samples for long periods to obtain the detection limits given in Table 5. For example, many samples contained larger amounts of copper than we had anticipated. It was not possible to reduce the intensity of copper x rays and maintain the required detection limits for lighter elements. The only solution was to reduce the proton beam intensity, thus preventing the counting rate of copper x rays from exceeding the practical limits of the electronic system. We also did not fully appreciate the significance of γ rays from sodium. Again, long runs were required to reduce the statistical uncertainty in the γ-ray background.

The characteristics of the sample have a major effect on detection limits in PIXE analysis. Limits for typical samples of a particular type can be given in the relatively simple form shown in Table 5. Simple statements of performance are appealing, but they are unrealistic when the technique is sensitive to many elements and sources of interference modify results. Since the goal of this program was to obtain the best possible detection limits for a wide range of elements, we have maintained the detection limits listed in Table 5 for the vast majority of samples. As described above, many samples required unexpectedly long bombardment periods; hence the actual cost of those analyses exceeded the charge made to the program.

If PIXE analysis is to be provided at fixed cost, the detection limits must be given in a more complex form than that used in Table 5. For example, factors should be included that account for the presence of high γ-ray background from elements, such as sodium, and intense x rays from common medium-weight elements, such as copper and zinc. Interference effects can be stated in a relatively simple form as illustrated by the effect of calcium

on scandium described in this work. However, if all conceivable possibilities of interference were included, the table of detection limits would be too long. A subjective judgement is needed to define the interferences which are likely to be significant in the analysis.

With any practical statement of detection limits, it is very difficult to obtain the desired results for some unusual samples. For example, in this program approximately 50 samples contained several ppm of mercury, a preservative, accidentally added when the samples were collected. A heavy element, such as mercury, emits 15 x rays which cover a wide energy range. When the concentration of mercury was several orders of magnitude larger than anticipated, it was essentially impossible to avoid x-ray interferences and an increase in the variability of the observations for other elements.

An important distinction should be made between PIXE and many other "multielemental" techniques. Although the computer program may be designed to look for selected x rays in the first phase of the analysis, <u>all</u> x rays detected from the sample are maintained in the x-ray spectrum. All optical emission techniques, claimed to be multielemental, retain only a limited portion of the emitted spectrum. Therefore unusual elements can not be added to the analysis after the sample has been processed. Not only is potentially valuable information lost, but it is impossible to recognize the presence of unusual elements which may interfer with the elements of interest. This is not the case with PIXE analysis. Unusual elements, whose concentrations exceed the detection limits, are added to the analysis and any variability caused by interference is evaluated.

SECTION 6

PROCEDURES AND QUALITY CONTROL USED IN THE ANALYSIS OF DRINKING WATER SAMPLES

The analysis for all elements heavier than calcium was made on targets prepared by vapor filtration from approximately 30-ml samples of drinking water. Each sample, contained in a polyethlene cubitainer, was shaken vigorously by hand before pouring an aliquot into the cylindrical tube of the vapor filtration apparatus. This procedure eliminated the possibility of contamination which could occur when graduated cylinders or pipets are used.

Each vapor filtration cylinder was calibrated so that the volume of sample in the cylinder could be determined from the height of the water column. Thirty ml of water were pipetted into each of the vapor filtration cylinders. The height of the water column was measured with a scale marked in millimeters. The scale rested on the collar at the bottom of the cylinder (see Figure 3). Each collar was machined to a tolerance of less than 0.1 mm so that the position of the scale was reproducible and the height of the column below the first mark on the scale was known. The total height of the water column in each cylinder was measured. The average height of a 30-ml column in 120 cylinders was 150 mm with a standard deviation of 1.5 mm. It is evident that the inside diameter of the cylinders (16 mm) is constant to approximately 1 percent.

A scratch mark was made on each cylinder at the 30-ml level as an aid in pouring a sample. However, the actual volume of the sample was measured by holding the millimeter scale at the side of the cylinder. The height of the column could easily be measured to within 1 mm. When this variability is combined with the standard deviation in the average height of a 30-ml column, the expected standard deviation of the measurement is less than 1.8 mm or 1.2 percent. Each mm on the scale corresponds to 0.2 ml of water; the measured height in mm was multiplied by 0.2 ml to obtain the sample volume.

In Section 4 we explained that one-ml samples were used for the analysis of elements lighter than scandium (Z = 21) to reduce the corrections required for the absorption of low energy x rays in the sample material. The water used for analysis of light elements was poured into a clean plastic beaker. One ml of water was transferred to the vapor filtration device with an Eppendorf pipet (Brinkmann Number 22-35-090-1). New pipet tips were cleaned with our standard procedure, described later in this section. Each tip was used one time, then discarded. Although the samples used in the analysis of light elements required more handling than those used in the analysis

heavy elements, the danger of contamination was negligible because the desired detection limits were 100 times higher than for heavy elements.

To evaluate the accuracy of the complete analytical procedure, an internal standard, 4 μg yttrium in one ml ultra-pure water, was added to each sample aliquot using an Eppendorf pipet. (The previously described precautions for the pipet tips were used.) The same quantity of yttrium tracer was added to all ultra-pure water samples processed as blanks. The role that the yttrium played in the analysis will be considered at several points in the subsequent discussion.

Occasionally a water leak would develop at the top of the cellophane film shortly after the sample was poured into the cylinder. Some targets were also lost when cellophane films broke on the pumping stations after the samples had dried. Sample preparation was scheduled to enable close observation at these times. A vacuum valve was included at each of the 120 pumping ports so that faulty samples could be isolated from the vacuum system.

All sample preparation, handling, and target storage was done in a pressurized clean room. The room had a single door and no windows. Air was pulled into the room through a high efficiency electrostatic filter (Trion Model TTM-II). The air intake was located underground in an air-conditioned part of the building; hence the input air to the filter was already relatively clean. The air pressure in the room was higher than in the outside hall so that air left the room when the door was opened. The water vapor pumps were located one floor below the clean room so there was no danger of the pumps causing sample contamination. The pumps were connected to the vapor filtration apparatus with a three-inch pipe passing through the floor of the clean room.

When the sample was dry, the cellophane film was removed from the vapor filtration device and mounted in a plastic frame. Since the film was precut to fit clamping ridges in the frame, only a few seconds were required to position the sample deposit in the center of the frame. The two halves of the frame were then snapped together and the finished target was stored in a covered plastic tray. When the targets were scheduled for bombardment they were transferred to circular plastic trays which fit the modified photography projector in the bombardment chamber (described in Section 3).

Standard solutions provided by the USEPA to check the quality of the analyses were handled in essentially the same way. The solutions were diluted with ultra-pure water according to the instructions provided with the standards. Normally, 30 ml of the diluted solution were used in the vapor filtration device. A smaller volume was used to prepare a few of the standards to minimize the damage to the cellophane by the aqua regia present in the solutions. At first 15 ml of the standard was prepared. If the target broke, then 5 ml was used. Targets, prepared from these smaller volumes, were bombarded for a longer period to obtain the desired detection limits for the heavier elements.

Several alternatives were tried before a satisfactory method was found for analyzing the 1.5-ml aliquots of acid preservative furnished by the USEPA. At first the 1.5-ml aliquot was diluted with one liter of ultra-pure water. With this dilution, very few elements were detected. Next, aliquots were diluted with 200 ml of ultra-pure water. Many of these targets broke because of the relatively high concentration of acid. Finally, aliquots were diluted with 500 ml of ultra-pure water to obtain durable targets having a two-fold weight increase in trace elements.

Targets prepared from 30-ml and 1-ml drinking water samples were bombarded with 4-MeV protons. The most intense x rays emitted were from calcium. In the analysis of the 30-ml samples, one-microampere (μa) beam current and a 0.8-mm thick mylar absorber were used. The latter absorbed the intense calcium x rays and provided optimum transmission for x rays from elements heavier than calcium. A 0.09-mm Mylar absorber and a 0.05-μa beam current were used for the analysis of elements lighter than scandium in one-ml samples. This absorber prevented scattered protons from reaching the x-ray detector, but it was sufficiently thin to permit silicon to be included in the analysis. Although the 1-ml sample had much less material than the 30-ml sample, a lower beam current was used since the calcium x-ray intensity was not reduced by the 0.09-mm Mylar filter.

The analysis of each 30-ml sample for elements heavier than calcium required 30 minutes to obtain the detection limits given in Table 5. The analysis time for elements lighter than scandium was only 5 minutes because less data was required to achieve the relatively higher detection limits.

Analyses were normally performed from 4 pm until 8 am the following morning. At the beginning of each 16-hour running period, several system tests were performed. A target having small chips of titanium, zinc, molybdenum, and tin metals was bombarded to provide a series of clean x-ray peaks covering the energy range of interest. The computer analyzed these peaks to determine the energy calibration of the system and to check the energy resolution of the detector. There was no significant change in the response of the detector over the two-year period of the measurements. The energy calibration of the system varied less than 0.01 percent.

As explained in Section 3, it was not necessary to remeasure a full set of calibration targets to check the x-ray yield calibration. One calibration target was analyzed at the beginning of each 16-hour analysis period to ensure that the proton charge-measuring system was operating correctly. The charge-measuring system proved to be very reliable and required maintenance only once in the two-year period. Once each week, calibration targets were used to ensure that absorption in the Mylar filters was unchanged. This test did not need to be performed more frequently because the buildup of material on the surface of the absorber was very slow. When the absorption had increased by 3 percent, the absorber was cleaned.

Although the system has proved to be extremely reliable, the possibility of intermittent failures was considered. The yttrium internal standard provided a running check on each analysis. A temporary failure in the charge-measuring system or the detector would immediately produce an *abnormal yield of yttrium x rays. The computer* checked the yttrium counting rate several times a minute and would stop the measurement and inform the operator if a problem developed. Almost all low yttrium yields could be traced to a failure in the target; either some of the sample was lost in the vapor filtration process, or the target was broken during bombardment. New targets had to be made for approximately 10 percent of the samples. A series of low yttrium yields and subsequent checks with calibration targets identified the one occurrence of failure in the charge-collection system.

At the beginning of the project, the calcium concentration in each sample was checked with an ion sensitive electrode so the volume of water poured into the vapor filtration device could be adjusted. However, since relatively few of the samples had sufficient calcium to require reduced volume targets for heavy element analysis, this procedure was discontinued. Instead, we adopted a standard procedure of analyzing approximately 30-ml samples. When a sample with high calcium concentration reached the data collection stage, the intensity of the proton beam was reduced to limit the x-ray counting rate. Although a large volume sample was used, the calcium still had the specified effect on detection limits because less data could be collected in the normal running period. Partial loss of the sample deposit from some of these targets during bombardment was easily recognized by a low yttrium yield. When this occurred, a new target was made from a 20-ml sample. Since we were handling thousands of targets and some of them had to be remade for other reasons, this was the most efficient method for routine handling of samples with high calcium concentrations.

The performance of the beam-switching system and the pile-up rejector was continuously monitored by the computer. The computer calculated the amount of pile-up that should occur from the observed counting rates of intense x rays. Any pile-up peaks statistically significant relative to the background were included in the least square fit to prevent mistakes from being made in the measurement of x-ray peaks. The computer compared the observed pile-up to that expected and notified the operator if the two rates did not agree. This procedure provided a running check on the pile-up detector and on the beam-pulsing system. If the beam was not being switched correctly, the probability of pile-up increased dramatically. The beam-switching system has required maintenance twice but the pile-up rejector has required no maintenance in the two-year running period.

The reproducibility of the analysis was evaluated periodically by analyzing multiple targets from typical samples. Since one-liter drinking water samples were provided for analysis, they could be used in the evaluation of precision. The procedure for obtaining and analyzing the targets was varied. For example, multiple targets were made at the same time for several samples. Sometimes these targets were analyzed immediately to evaluate the instrumental contribution, s_i, to the standard deviation (discussed in Section 5). Elements present in relatively high concentrations were used so that the variations

due to counting statistics were not a significant factor in the standard deviation. On other occasions, the multiple targets were held for four weeks and then analyzed. This procedure evaluated the stability of the targets and served as a continuing check on s . To evaluate the consistency of the target-making procedure, aliquots of some special solutions were prepared on a weekly basis. The analytical observations of these samples were averaged and the coefficient of variation was calculated. Typical results for tests of this type have been given in Table 3. Throughout the course of this contract, the average percent coefficient of variation for repeated analyses was approximately 10.

One of our most difficult tasks has been to establish and maintain procedures which would minimize incidences of sample contamination. Prevention of contamination was an important goal in the development of the vapor filtration technique. It was also essential that the samples be prepared in a very clean environment such as the clean room described previously in this section. An ample supply of ultra-pure water was also necessary to clean apparatus, to prepare standard solutions, and to evaluate cleaning procedures.

Ultra-pure water was provided by a system obtained from Culligan Corp. The Physics Department distilled water supply was used as the input for the ultra-pure water system. The total dissolved solids in the input water were less than 10 ppm. The water passed through a carbon filter tank (Cullar-F, 1618-00), two mixed bed ion exchange tanks (Model 2603-26) and finally through a submicron filter (Model 9095-76). The resistance of the water, continuously monitored by a built-in meter, was always greater than 16 megohms. Since distilled water was used for the input of the ultra-pure water system, component replacement was required only at three-month intervals.

Several 30-ml samples of ultra-pure (non-acidified) water were analyzed once a month. The number of targets, average elemental observations, and the corresponding standard deviations for a typical three-month period are given in Table 6. There was some variation in the quality of the ultra-pure water. The concentrations of 70 of the 76 elements were less than the detection limits. The most abundant element was iron while nickel, copper, zinc, cadmium, and lead were sometimes present in significant concentrations. In this example, the concentrations were higher during the middle of the period than at the beginning or end. No general pattern was found for the variation in concentrations. This ultra-pure water was more than adequate for cleaning purposes since only a few drops of water were left in the vapor filtration devices at the end of the cleaning cycle.

It was difficult to evaluate the occurrence of contamination at very low elemental concentrations. The ultra-pure water used to evaluate contamination was acidified so the conditions during the vapor filtration process were approximately the same as during the preparation of drinking water samples. Some low-level impurity in the acid and ultra-pure water was inevitable, so it was impossible to measure contamination satisfactorily. The best available technique was to make replicate targets from the same acidified ultra-pure water. The trace elements in the acidified ultra-pure water should have been consistent from target to target, but there could have

TABLE 6. TRACE ELEMENTS IN ULTRA-PURE WATER

Element	Sample 1		Sample 2		Sample 3	
	Average* ppb	Standard deviation ppb	Average† ppb	Standard deviation ppb	Average* ppb	Standard deviation ppb
Cr	0.31	0.11	0.12	0.10	0.40	0.20
Fe	6.8	1.5	8.1	2.0	6.1	1.8
Ni	0.21	0.10	0.36	0.15	0.26	0.10
Cu	0.9	0.5	1.3	0.8	< 0.5	
Zn	< 0.5		2.5	1.0	1.0	0.8
Cd	0.22	0.12	0.50	0.32	< 0.1	
Pb	0.31	0.22	0.40	0.33	1.10	0.20

*Average of three target analyses.

†Average of five target analyses.

been considerable variation in the contamination. If the observed variations were consistent with the expected standard deviation, then the contamination was either negligible or constant. We expect the most likely source of contamination was airborne particles that would not produce a constant contamination level.

Ultra-pure water was a better solution for contamination tests than a standard solution with known elemental concentrations. The instrumental variation was usually negligible for the ultra-pure water analyses, but its significance would increase with the elemental concentration. A 2-ppb contamination in ultra-pure water would be much easier to detect than the same contamination in a solution containing 20 ppb of the element.

A set of six vapor filtration devices were assigned for use with acidified ultra-pure water. No other type of sample was placed in these devices. The devices were originally cleaned with a 10 percent nitric acid solution. They were rinsed with ultra-pure water before each test sample was processed. These devices were randomly placed on the pumping apparatus, and 30 ml of acidified ultra-pure water were processed at the same time that regular samples were being processed. Thus the probability of contaminating these targets with airborne particles was the same as for regular samples. The results for a typical evaluation of this type are given in Table 7.

TABLE 7. ACIDIFIED ULTRA-PURE WATER ANALYSES USED TO EVALUATE CONTAMINATION

Element	Observations (ppb) 1	2	3	4	5	6	Average ppb	Standard deviation ppb
Cr	< 0.1	0.2	< 0.1	< 0.1	0.3	< 0.1	--	--
Fe	17.0	14.0	9.5	10.0	15.0	11.0	12.8	3.0
Ni	0.21	0.27	< 0.10	0.31	0.28	0.20	0.25	0.05
Cu	1.3	1.7	0.9	2.1	1.4	3.3	1.8	0.8
Zn	3.1	2.2	1.6	3.6	2.0	1.8	2.4	0.8
Cd	0.15	0.46	0.15	0.28	0.30	0.35	0.30	0.10
Pb	0.9	0.5	1.1	1.0	1.3	0.8	0.9	0.3

The observed standard deviation for nickel, copper, zinc, and cadmium were smaller than the expected standard deviation (0.1, 1.0, 1.0, and 0.1, respectively), so contaminations from these elements were either negligible or constant. In four out of six targets the chromium concentration was less than the detection limit. The analysis of the other two targets showed a low level of chromium contamination.

A lead concentration of 1 ppb with a standard deviation of 0.2 ppb was observed in the cellophane target backing material. The average lead concentration shown in Table 7 was essentially the same as that in the cellophane but the standard deviation here was slightly larger. Since several ppb lead were observed in most drinking water samples, small variations should not have a major effect on the interpretation of lead analyses.

The vapor filtration devices had to be thoroughly cleaned to avoid contamination. The first step in cleaning the devices was a 30-minute rinse with flowing distilled water in a siphon-type pipette washer made of polyethylene. (Made by Nalgene Company; Cole-Parmer stock numbers 6190 washer-rinser and 6155 basket.) Next, the devices were soaked for 30 minutes in 10 percent nitric acid. The tank used for the nitric acid soak was located under a hood to prevent acid vapor from attacking metal surfaces in the clean room. The final rinse was for 30 minutes in flowing ultra-pure water. Water droplets were shaken off and the devices stored in covered polyethylene trays. The devices were not dried prior to storage. There was probably much less contamination from having a few drops of ultra-pure water left in the device than from leaving the devices open to air for a long drying period. As stated previously, all handling and storage were confined to the clean room.

The cleaning procedure was thoroughly tested before drinking water analysis began. The vapor filtration devices were contaminated by processing solutions containing large concentrations of the elements of primary interest (Table 2). The devices were cleaned with the procedure described above. Then targets were made by processing 30 ml of acidified ultra-pure water through the devices. No measurable contamination was observed in the vapor filtration devices.

Since it was possible that the vapor filtration devices became more difficult to clean as they were used, similar tests were continued during the drinking water analyses. When a set of regular samples was being put on the pumping manifold, six devices, selected randomly, were checked for contamination. These devices previously had been used with regular samples and cleaned by the standard procedure. Targets were made from 30-ml aliquots of acidified ultra-pure water. The analyses for a typical set of these targets are shown in Table 8 and they are statistically indistinguishable from the results in Table 7. The same solution was used for the two tests,

TABLE 8. EVALUATION OF CLEANING PROCEDURES FOR VAPOR FILTRATION DEVICES

Element	Observations (ppb) 1	2	3	4	5	6	Average ppb	Standard deviation ppb
Cr	0.25	< 0.1	< 0.1	< 0.1	0.20	< 0.1	--	--
Fe	14	21	12	10	13	17	14.5	4.0
Ni	0.19	0.21	0.30	0.15	0.24	0.27	0.23	0.05
Cu	2.1	1.8	3.1	2.9	2.4	2.3	2.4	0.5
Zn	2.7	2.0	3.3	2.2	2.8	3.6	2.8	0.6
Cd	0.25	0.1	0.15	0.31	0.33	0.27	0.24	0.1
Pb	1.1	1.3	0.7	1.0	0.9	0.8	1.0	0.2

but the vapor filtration devices used to obtain the results in Table 7 were only used with ultra-pure water. Thus, any contamination left in the vapor filtration devices during the washing process was too small to be measured.

One source of unexpected contamination was observed. Field personnel, associated with the cardiovascular disease study, collected a number of drinking water samples at each site for determination of a variety of inorganic constituents by several laboratories. Unfortunately, a number of samples were either incorrectly preserved or the samples were not sent to the correct laboratory. As a result, the Purdue Accelerator Laboratory received about 50 samples preserved with mercuric chloride ($HgCl_2$). The pH of the incoming samples was measured to detect the absence of nitric acid, the preservative for the trace element analyses. These measurements did not

reveal, however, the accidental preservation of a sample with both mercuric chloride and nitric acid. A target with large quantities of mercury would contaminate other targets in the bombardment chamber at the same time. It was necessary to make new targets for many samples to determine whether mercury was really present in the original drinking water. Although a determined effort was made to check cases that were suspicious, it is possible that some of our reports for mercury are high due to contamination. Since mercury was not one of the elements of primary interest in this investigation, we did not evaluate the probability of mercury loss during bombardment when mercury was present at trace levels.

Five copies of a computer printout of the results of each analysis were forwarded to the USEPA project oficer. The results of all analyses were also recorded on computer magnetic tape for statistical evaluation by the USEPA staff.

The original data and analyses were stored on magnetic tape and will be held at the Purdue Accelerator Laboratory until May 1, 1978. The analysis of any sample can be re-examined by reading the data and analysis parameters back into the computer. The remainder of each sample has been retained in its original container and will be stored at the Purdue Accelerator Laboratory until May 1, 1978. The targets have not been retained.

SECTION 7

ANALYSIS FOR SODIUM USING ATOMIC ABSORPTION

Plastic labware was used in the preparation and storage of all solutions to avoid contamination with sodium, often observed with the use of glass. The labware was washed using a tap water rinse, followed by one percent nitric acid bath and then two washes in deionized water. Blanks were prepared by filling some of the washed sample bottles with deionized water and analyzing them in the same manner as regular water samples. The concentration of sodium in the blanks was always less than 0.25 ppm, indicating that the cleaning procedure was satisfactory.

Nalgene flasks and Eppendorf pipets were used in the preparation of standard solutions. Appropriate aliquots of Fisher Scientific Company sodium atomic absorption standard were diluted with deionized water. A 100-ml aliquot of each drinking water sample was transferred from the cubitainer to a small plastic bottle and stored at room temperature until the sodium analysis was performed.

A Perkin Elmer Model 306 spectrophotometer with deuterium background correction was employed for all measurements. The instrument was operated in the absorption mode with an air-acetylene flame. Samples containing more than 2.5 ppm sodium were analyzed using the 330.2-nm line, a three-slot Boling burner, an air flow of 23.2 liters per minute, and an acetylene flow of 7.6 liters per minute. A set of six sodium standards with concentrations of 3.13, 6.25, 12.5, 25, 50, and 100 ppm were run before and after each set of measurements (100 or less samples per set). A linear least-squares fit of the observations was performed to obtain a calibration graph. The standards were also run singly during a set of measurements for quality control purposes. If the concentration of the sodium in a drinking water sample exceeded 100 ppm, the sample was diluted by a factor of ten using an Eppendorf pipet and a Nalgene flask and the analysis was repeated.

Samples containing less than 2.5 ppm sodium were analyzed using the 589.6-nm line, a nitrous oxide burner, an air flow of 9.2 liters per minute, and an acetylene flow of 5.8 liters per minute. Five solutions with sodium concentrations of 0.25, 0.5, 0.75, 1.0, and 2.0 ppm were used for standardization and quality control in the manner described previously.

Twelve drinking water samples were selected to evaluate the reproducibility of the analyses. Six aliquots of each sample were analyzed. The average of the six analyses of each sample and the standard deviation of the measurements are presented in Table 9.

TABLE 9. PRECISION OF ATOMIC ABSORPTION MEASUREMENTS OF SODIUM IN DRINKING WATER SAMPLES

Average* concentration (ppm)	Standard deviation (ppm)
53.5	1.33
53.1	1.59
24.1	0.93
23.7	0.93
19.3	1.1
18.6	1.6
18.3	0.9
12.6	1.4
11.8	1.8
8.6	1.3
9.2	1.8
4.8	0.9

*Average of six determinations.

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